STRUCTURES, REACTIVITIES, AND MECHANISMS OF SODIUM AND BORON OXAZOLIDINONE-DERIVED ENOLATES

A Dissertation
Presented to the Faculty of the Graduate School
of Cornell University
In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Zirong Zhang
August 2019

STRUCTURAL, MECHANISTIC AND REACTIVITY STUDY OF OXAZOLIDINONE ENOLATES

Zirong Zhang, Ph. D.
Cornell University 2019

The soft enolization of an acylated oxazolidinone using di-*n*-butylboron triflate (*n*-Bu_2BOTf) and trialkylamines and subsequent aldol addition was probed structurally and mechanistically using a combination of IR and NMR spectroscopies. None of the species along the reaction coordinate shows a penchant for aggregating. Complexation of the acylated oxazolidinone by *n*-Bu_2BOTf was too rapid to monitor, as was the subsequent enolization with Et_3N (triethylamine). The pre-formed *n*-$Bu_2BOTf{\cdot}Et_3N$ complex displaying muted Lewis acidity and affiliated tractable rates reveals a rate-limiting complexation via a transition structure with a complicated counterion. *n*-$Bu_2BOTf{\cdot}$*i*-Bu_3N bearing a hindered amine shifts the rate-limiting step to proton transfer. Rate studies show that the aldol addition with isobutyraldehyde occurs as proffered by others.

Oxazolidinone-based sodiated enolates (Evans enolates) were generated using sodium diisopropylamide (NaDA) or sodium hexamethyldisilazide (NaHMDS) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), (*R,R*)-*trans*-*N,N,N′,N′*-tetramethylcyclohexanediamine [(*R,R*)-TMCDA], or (*S,S*)-TMCDA. ^{13}C NMR spectroscopic analysis in conjunction with the method of continuous variations (MCV) and density functional theory (DFT) computations revealed the enolates to be octahedral *bis*-diamine-chelated monomers. Rate and computational studies of an alkylation with allyl bromide implicate a *bis*-diamine-chelated-monomer-based transition structure. The sodiated Evans enolates form mixed dimers with NaHMDS, NaDA, or sodium 2,6-di-*tert*-butylphenolate, the reactivities of which are examined. Stereoselective quaternizations, aldol additions, and azaaldol additions of sodiated Evans enolates are described.

[2,3]-Sigmatropic rearrangements (Wittig rearrangements) of α-alkoxy oxazolidinone enolates are described. Whereas alkali metal enolates fail owing to facile

deacylation, boron enolates generated from di-*n*-butylboron triflate and triethylamine rearranged in good yields and high selectivities with exceptions noted. IR and NMR spectroscopies show the boron was chelated by the α-alkoxy group rather than the more distal oxazolidinone carbonyl in the complex and enolate. The rearrangement product contained a boron alkoxide that remained unchelated by either carbonyl. Optimization was guided by density functional theory computations suggesting that valine-derived oxazolidinones would be superior to the phenylalanine-derived analogs.

BIOGRAPHYCAL SKETCH

The author was born on February 2, 1994 in Binhai, China. After receiving one year of secondary education at Shenzhen Middle School, she attended the Special Class for the Gifted Young at University of Science and Technology of China. Under the guidance of Prof. Yao Fu, she worked on copper-catalyzed decarboxylative cross coupling reactions. The author received her B.S. in Chemistry after defending her thesis in June 2014. Later that year, she began her graduate studies at Cornell University in the laboratory of Prof. David B. Collum. Her graduate work focused on structures, reactivities, and mechanism on oxazolidinone enolates, including mechanisms underlying boron enolates aldol addition, structures and reactivities of sodiated enolates, and Wittig rearrangement of boron enolates. The author received a M.S. in 2016 and a Ph. D. in August 2019.

This work is dedicated to my parents,
Xiaoyu and Jili

ACKNOWLEDGMENTS

First of all, I would like to acknowledge my advisor, Prof. David B. Collum, for his forethoughtful guidance, genuine support, and gracious patience in my graduate research. He has brought enormous enthusiasm and delight into both my chemistry studies and daily life. My sincere gratitude also goes to special committee members Prof. Geoffrey W. Coates and Prof. Brett P. Fors, who have provided hearty encouragements and creative insights. I'd also like to thank Prof. Phillip J. Milner for acting as Prof. Fors' proxy for my B exam.

It is a great pleasure to work in the Collum group with all the wonderful labmates. Research associate Dr. Yun Ma, postdoctoral associate Dr. Gabriel J. Reyes-Rodríguez, and fellow graduate students Dr. Kyong Joo Jin, Dr. Evan H. Tallmadge, Dr. Michael Houghton, Ms. Jacqueline Perodeau, Dr. Kyle A. Mack, Mr. Ryan Woltornist, Mr. Jackson Clark, and especially Dr. Russell F. Algera, Dr. Janis Jermaks, and Dr. Yuhui Zhou have all contributed to the completion of this work.

The department of Chemistry and Chemical Biology at Cornell University is a very inspiring and friendly place to work in. The faculty, staff, and many graduate students and postdoctoral associates in other groups provided solid support for my research. Dr. Ivan Keresztes at the NMR facility has been of tremendous help.

Finally, I would like to thank my family and friends. I am very grateful to my parents, Mrs. Xiaoyu Sun and Mr. Jili Zhang, as their invaluable support accompanied and encouraged me throughout my educational career. The friendship and endorsement from Dr. Yuhui Zhou, Dr. Ying Zhang, and Dr. Lu Zhang are irreplaceable as well.

TABLE OF CONTENTS

CHAPTER 1

EVANS ENOLATE: STRUCTURES AND MECHANISMS UNDERLYING THE ALDOL ADDITION OF OXAZOLIDINONE-DERIVED BORON ENOLATES

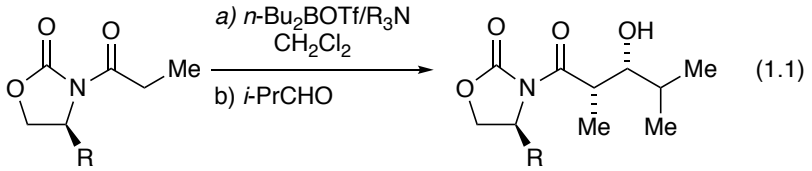
Evans Enolates: Structures and Mechanisms Underlying the Aldol Addition of Oxazolidinone-Derived Boron Enolates

Abstract

The soft enolization of an acylated oxazolidinone using di-*n*-butylboron triflate (*n*-Bu_2BOTf) and trialkylamines and subsequent aldol addition was probed structurally and mechanistically using a combination of IR and NMR spectroscopies. None of the species along the reaction coordinate shows a penchant for aggregating. Complexation of the acylated oxazolidinone by *n*-Bu_2BOTf was too rapid to monitor, as was the subsequent enolization with Et_3N (triethylamine). The pre-formed *n*-$Bu_2BOTf{\cdot}Et_3N$ complex displaying muted Lewis acidity and affiliated tractable rates reveals a rate-limiting complexation via a transition structure with a complicated counterion. *n*-$Bu_2BOTf{\cdot}$*i*-Bu_3N bearing a hindered amine shifts the rate-limiting step to proton transfer. Rate studies show that the aldol addition with isobutyraldehyde occurs as proffered by others.

Introduction

During the development of polyketide total syntheses and the emergence of biomimetic aldol additions, few reagents have been as central as the oxazolidinone enolates, colloquially referred to as Evans enolates.[1] In their seminal 1981 paper, Evans and co-workers[2] showed that the acylated oxazolidinone scaffold controls additions with high facial selectivity. Although their first attempts likely involved alkali metal enolates, boron enolates derived from di-*n*-butylboron triflate[3] (*n*-Bu_2BOTf) provide exceptional diastereoselectivities (eq 1.1).[4] Since that first publication, Evans enolates have been reported in an astonishing 1600 patents.[5]

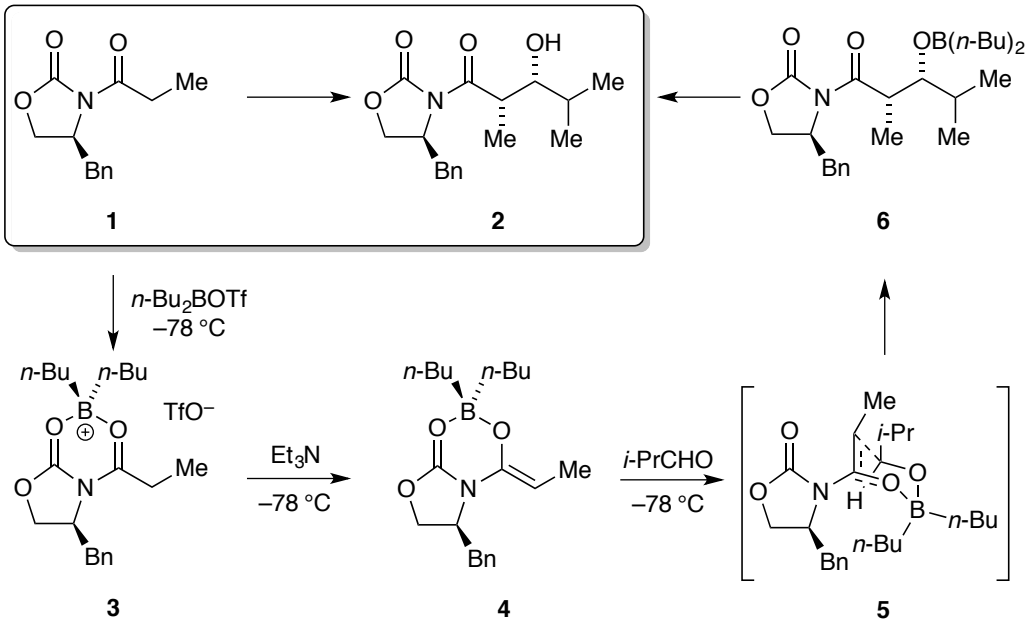


(1.1)

Boron enolates, including several derived from oxazolidinones,[6] have been examined crystallographically,[7] spectroscopically,[7,8] and computationally.[9,10] By contrast,

few experimental probes of mechanism have been carried out with either simple boron enolates[11] or oxazolidinone-based variants.[6,12–15] On the heels of investigations of lithium-based aldol additions of Evans enolates,[12] we undertook structural and mechanistic studies of the boron variant in Scheme 1.1.[16]

Scheme 1.1. Mechanism of oxazolidinone-based aldol addition.



Results

Structure Determinations: General Strategies. The aldol addition was carried out as prescribed in the literature;[2] however, $CHCl_3$ was used interchangeably with CH_2Cl_2 owing to the convenience of $CDCl_3$ for ^1H and ^{13}C NMR spectroscopies. ^{11}B NMR spectroscopy was ineffectual owing to broad, poorly resolved resonances. IR spectroscopy, by contrast, proved particularly informative; carbonyl absorbances of key species are summarized in Table 1.1. Representative IR spectra are contained in Figure 1.1. ^1H and ^{13}C NMR spectroscopies were used to confirm the structures of key species.

Table 1.1. IR Absorbances of Key Intermediates[a]

Compd	C=X (cm^{-1})	
1	1777	1704
2	1777	1704
3	1727[b]	
4	1706	1658
6	1777	1704

[a]1777 and 1704 correspond to the oxazolidinone and propionyl group carbonyls, respectively.[14,15] [b]Superimposed single absorbance.

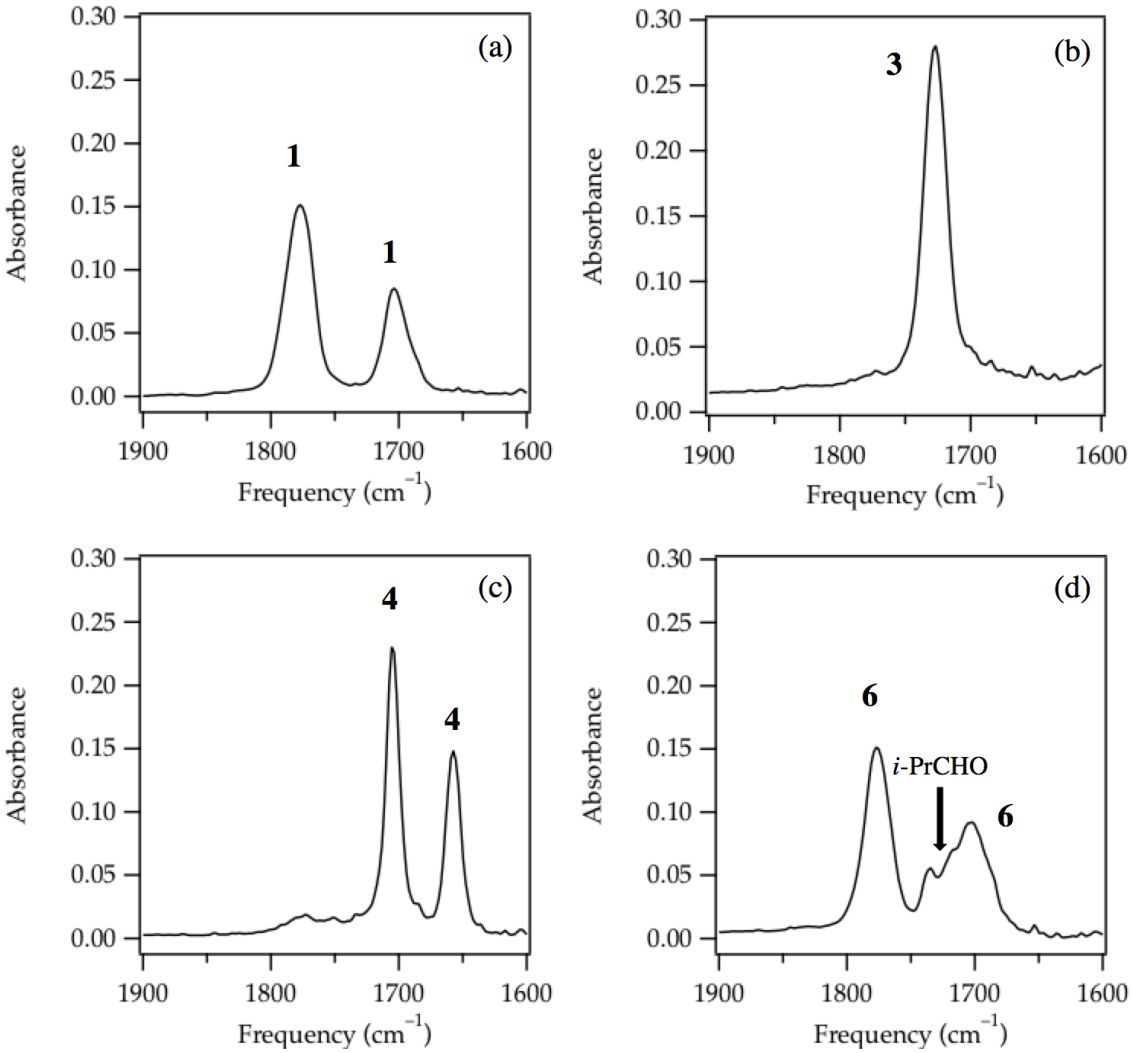
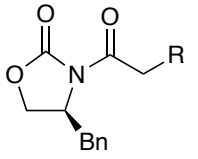


Figure 1.1. IR spectra of 0.10 M **1** in $CHCl_3$ recorded at –60 °C with (a) no additive, (b) 0.11 M *n*-Bu_2BOTf affording **3**, (c) 0.11 M *n*-Bu_2BOTf and 0.12 M Et_3N affording **4**, and (d) 0.11 M *n*-Bu_2BOTf, 0.12 M Et_3N, and 0.13 M *i*-PrCHO affording **6**.

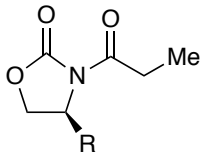
The method of continuous variations (MCV) was used to ascertain whether key intermediates associate into higher aggregates that would otherwise go undetected with standard spectroscopic methods.[17] If boron enolates are dimeric in solution, binary mixtures of two structurally related enolates would contain homodimers, $\mathbf{A_2}$ and $\mathbf{B_2}$ and a heterodimer, **AB** (eq 1.2). **AB** would appear as a new species or, in the event of rapid exchange, elicit changes in time-averaged ^1H or ^{13}C NMR chemical shifts. In the event, numerous binary mixtures of complexes (**3**), enolates (**4**), or alkoxides (**6**) derived from substrates in Chart 1.1 showed no evidence of **AB**.

$$\mathbf{A_2} + \mathbf{B_2} \rightleftharpoons 2\ \mathbf{AB} \qquad (1.2)$$

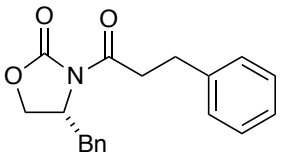
Chart 1.1. Enolate precursors



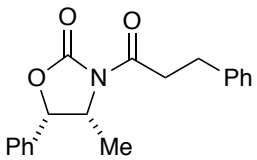
1; R = Me
7; R = H
8; R = *t*-Bu



9; R = *i*-Pr
10; R = Ph
11; R = $CH(Ph)_2$



12

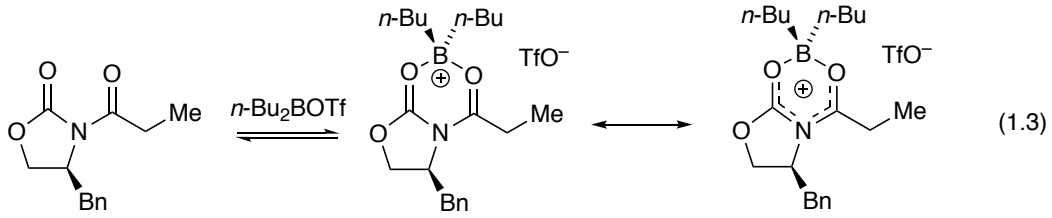


13

Complexation. The addition of 1.0 equiv of *n*-Bu_2BOTf to oxazolidinone **1** (0.10 M in $CHCl_3$) at 20 °C resulted in approximately 50% consumption of **1** and the appearance of a single new absorbance at 1727 cm^{-1} corresponding to complex **3**. We

suspect that the electron distribution exemplified by resonance structure **3a** (eq 1.3) accounts for the single C=X absorbance.

The reaction was instantaneous but not quantitative. Complete complexation was observed when the samples were either cooled with 1.1 equiv *n*-Bu_2BOTf to –60 °C or combined with >3.0 equiv of *n*-Bu_2BOTf at 20 °C (*vide infra*).

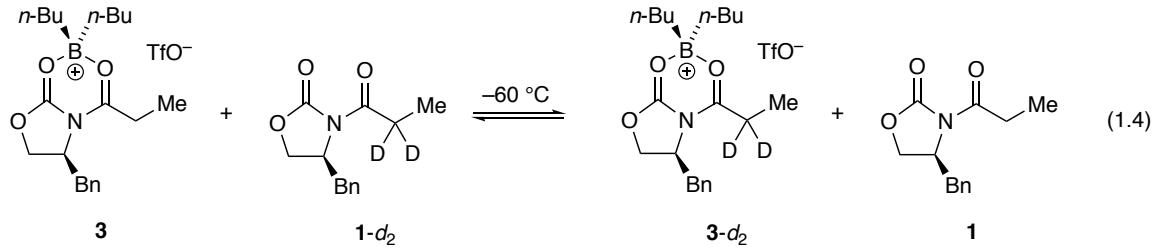


1 **3** **3a** (1.3)

favored at low temperature

^{1}H NMR spectroscopy showed the two diastereotopic protons of the propionyl methylene fragment in **3** as doublets of quartets with markedly different chemical shifts (d 3.0 and 1.7 ppm). In partially complexed samples containing only 1.0 equiv *n*-Bu_2BOTf, the upfield resonance appeared at 1.7 ppm at 20 °C and shifted to 1.4 ppm at –60 °C. It would be tempting to ascribe this result to complexation promoted at low temperature, but the shift occurred independent of the *n*-Bu_2BOTf concentration, which also promoted complexation. We suspect that the temperature dependence stems from an aromatic p-interaction with the proximate a-proton.[18,19] The analogous complex derived from **9**, which bears an isopropyl moiety, showed no anomalous shifting of the proximate a proton. Density functional theory (DFT) computations[20] for **3** with geometries optimized at the B3LYP/6-31G(d) level and corrected by single-point calculations at the MP2/6-31G(d)//B3LYP/6-31G(d) level did *not* support a proton–arene interaction.

Slow exchange on ^{1}H and ^{13}C NMR timescales made the two magnetically inequivalent *n*-butyl groups of **3** discernible. The treatment of complex **3** with **1**-d_2 showed rapid incorporation at –60 °C on ^{1}H NMR spectroscopy (eq 1.4), confirming that exchange was fast on laboratory timescales.



(1.4)

The results of ^{19}F NMR spectroscopy at –60 °C showed a single resonance (d –77 ppm) consistent with a free triflate ion that shifted downfield with additional *n*-Bu_2BOTf. By comparison, CF_3SO_3H and *n*-Bu_2BOTf displayed ^{19}F resonances at –79 and –76 ppm, respectively. The triflate counterion story becomes much more complicated.

Enolization. Adding triethylamine (Et_3N; 1.2 equiv) to solutions containing >95% complex **3** (1.1 equiv *n*-Bu_2BOTf, –60 °C) afforded enolate **4** instantaneously and quantitatively, as shown by the replacement of the absorbance of **3** with two new C=X absorbances (Table 1.1). Chelation by the oxazolidinone carbonyl was evidenced by the lower energy carbonyl absorbance at 1706 cm^{-1} (Table 1.1). The magnetically inequivalent *n*-butyl moieties of **4**, however, were time-averaged in the ^1H and ^{13}C NMR spectra at –60 °C, suggesting weak chelation.

Tandem Complexation–Enolization. The complexation of **1** to form **3** was too fast to monitor, as was the enolization of **3** to form enolate **4**. However, **1** reacted with a preassociated *n*-$Bu_2BOTf{\cdot}Et_3N$ complex at 0 °C at tractable rates with no detectable pre-complex **3** owing to the attenuated (inhibited) Lewis acidity.[21] *n*-$Bu_2BOTf{\cdot}Et_3N$ reacted in slow exchange with free Et_3N, and the ^1H NMR spectra confirmed the 1:1 complex noted previously.[22,23]

Rate studies revealed both expected and decidedly unexpected results. The conversion of **1** to enolate **4** at 0 °C under pseudo-first-order conditions (0.0020 M **1**) followed a first-order decay as confirmed by pseudo-first-order rate constants (k_{obsd}) that were independent of the concentration of **1**. Comparing **1** and **1**-d_2 afforded no isotope effect ($k_H/k_D = 1.00 \pm 0.01$). Post-rate-limiting enolization was confirmed by two additional experiments.[24] A mixture of pre-formed complexes **3** and **3**-d_2 (1.0 equiv each) was treated with a deficiency (0.80 equiv) of Et_3N, thereby forcing the instantaneous deprotonation to select H over D. The selective loss of **3** monitored with ^1H NMR

showed a large competitive isotope effect (k_H/k_D = 10). To confirm that the deprotonation of **3** was faster than decomplexation—a requirement for post-rate-limiting proton transfer[24]—we added low concentrations of an equimolar mixture of **1**-d_2 and Et_3N to a solution of **3**. Enolization proceeded to the exclusion of the exchange of **1**-d_2 into **3**. Conversely, adding low concentrations of an equimolar mixture of **1** and Et_3N to a solution of **3**-d_2 again resulted in dominant enolization, with approximately 10% incorporation of **1** into complex **3**-d_2. Slowing the isotopically sensitive enolization 10-fold relative to exchange with substrate revealed a 10% competing back reaction, which would have gone undetected in a measured isotope effect.[24]

A plot of k_{obsd} versus Et_3N concentration in excess showed an approximate inverse-first-order dependence (n = –0.9 ± 0.1) consistent with the reversible loss of the amine from *n*-$Bu_2BOTf{\cdot}Et_3N$ (Figure 1.2). Quite unexpectedly, a plot of k_{obsd} versus *n*-$Bu_2BOTf{\cdot}Et_3N$ concentration in which the excess amine concentration was held constant showed a *third-order dependence* (n = 3.3 $\pm$ 0.3; Figure 1.3). We neither anticipated this result nor have a fully satisfactory explanation, as discussed below.

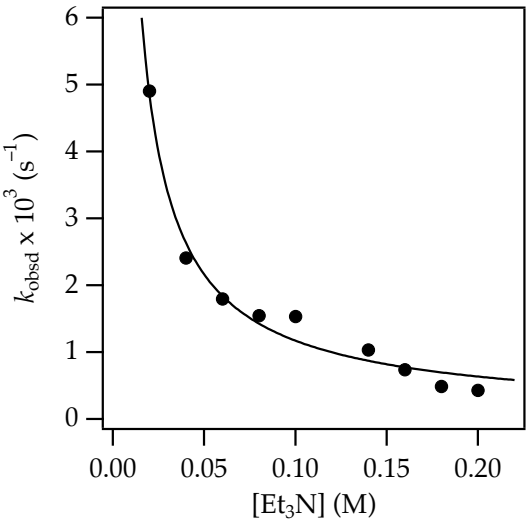


Figure 1.2. Plot of k_{obsd} versus added Et_3N concentration for the enolization of **1** (0.0020 M) by *n*-$Bu_2BOTf{\cdot}Et_3N$ (0.040 M) in $CHCl_3$ at 0 °C. $y = ax^b$, a = 0.00015 ± 0.00003, b = –0.88 ± 0.05.

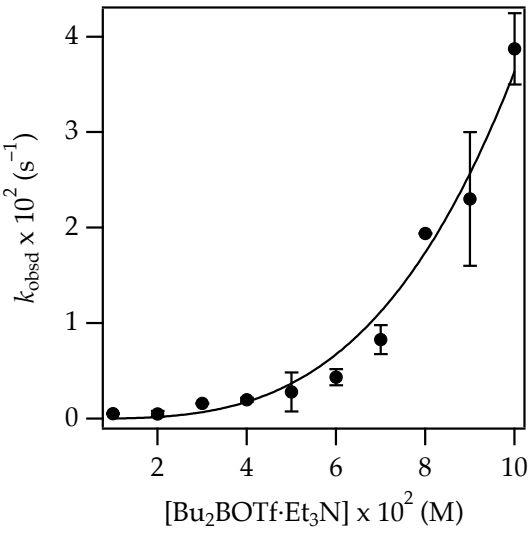


Figure 1.3. Plot of k_{obsd} versus *n*-$Bu_2BOTf{\cdot}Et_3N$ concentration for the enolization of **1** (0.0020 M) by 0.10 M free (uncomplexed) Et_3N in $CHCl_3$ at 0 °C. $y = ax^b$, $a = 72 \pm 3$, $b = 3.3 \pm 0.3$.

$$-d[\mathbf{1}]/dt = k'[\mathbf{1}][n\text{-}Bu_2BOTf{\cdot}Et_3N]^3[Et_3N]^{-1} \qquad (1.5)$$

Taken together, the reaction orders afforded the rate law in eq 1.5, which implicated a transition structure with $[(\mathbf{1})(n\text{-}Bu_2BOTf)_3(Et_3N)_2]^{‡}$ stoichiometry.[25] The triflate-based counterion denoted as "X^-" at the transition state would necessarily be complicated. Neither of the two amines in the rate-limiting transition state served as a Brønsted base because the deprotonation is post-rate-limiting. We defer the interpretation of stoichiometry to the discussion; however, we probed the amine dependence and obtained the following relative reaction rates: Me_2NEt (DMEA) < $MeNEt_2$ < Et_3N < *i*-Pr_2NEt < *i*-Bu_3N.

i-Bu_3N shifted the equilibrium to non-limiting behavior that has the effect of shifting the rate-limiting step to proton transfer as described by Scheme 1.2 and eqs 1.6–1.9. A plot of k_{obsd} versus *i*-Bu_3N concentration showed saturation kinetics (Figure 1.4) in which substrate and *i*-Bu_3N competitively coordinate to boron. K_{eq} was commensurate with a value measured with ^1H NMR using enolization-resistant isobutyrate **20** (see below) as a surrogate. The enolization of **1** using *i*-Bu_3N showed rate-limiting proton

transfer, as evidenced by a large kinetic isotope effect (k_H/k_D = 10) at low and high amine concentrations. Changing the addition sequence by adding *i*-Bu_3N to the substrate–boron complex provided the same behavior. The counterintuitive normal (rather than inverse) saturation owing to an unproductive side equilibrium stemmed from the dual role of amine as both inhibiting Lewis base and accelerating Brønsted base.

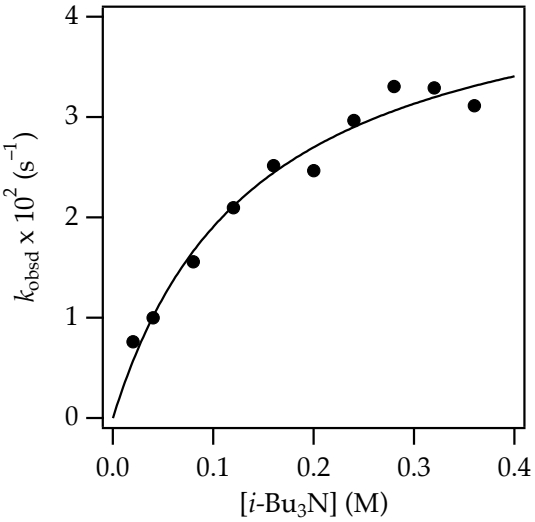
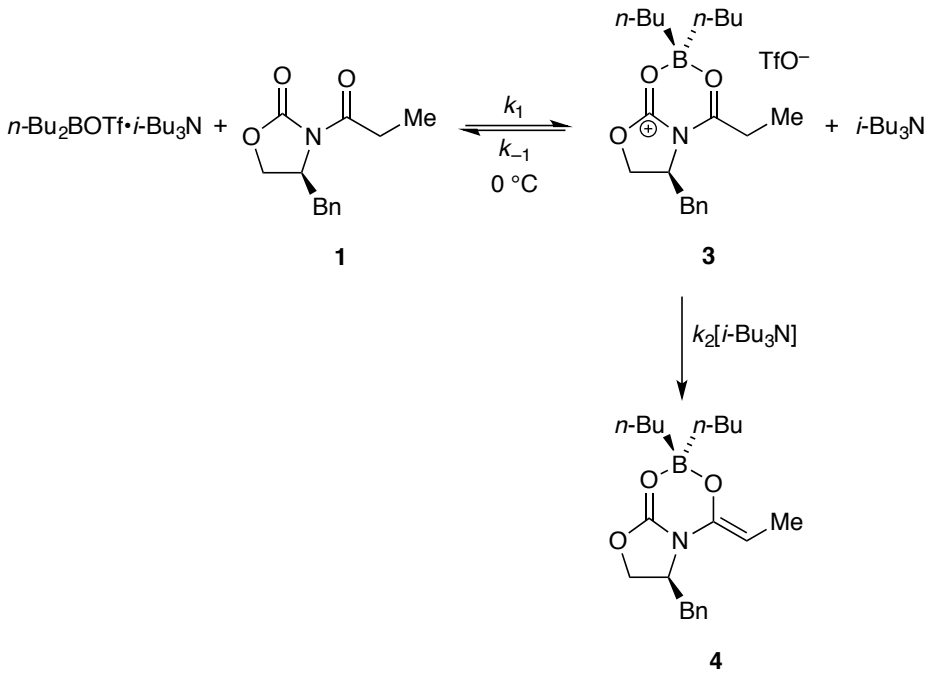


Figure 1.4. Plot of k_{obsd} versus *i*-Bu_3N concentration for the enolization of **1** (0.0020 M)by *n*-Bu_2BOTf·*i*-Bu_3N (0.040 M) and *i*-Bu_3N in $CHCl_3$ at 0 °C. $y = ax/(x + b)$, a = 0.046 ± 0.004, b = 0.14 ± 0.03.

Scheme 1.2. Competitive amine-mediated complexation and enolization.



$$d[\mathbf{4}]/dt = k_{obsd}[\mathbf{1}_{total}] \tag{1.6}$$

$$k_{obsd} = k_2 K_{eq}[n\text{-Bu}_2\text{BOTf}\cdot i\text{-Bu}_3\text{N}]/ \{1+K_{eq}[n\text{-Bu}_2\text{BOTf}\cdot i\text{-Bu}_3\text{N}]/[i\text{-Bu}_3\text{N}]\} \tag{1.7}$$

Low Amine Concentration

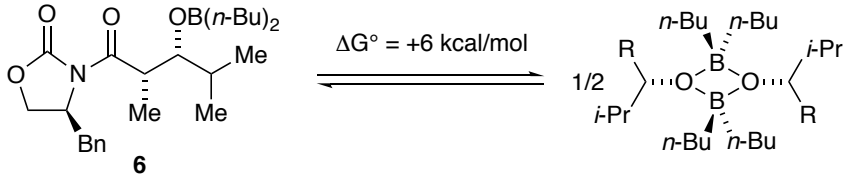
$$k_{obsd} = k_2[i\text{-Bu}_3\text{N}] \tag{1.8}$$

High Amine Concentration

$$k_{obsd} = k_2 K_{eq}[n\text{-Bu}_2\text{BOTf}\cdot i\text{-Bu}_3\text{N}] \tag{1.9}$$

Aldol Addition. The reaction of enolate **4** (0.10 M) and excess Et_3N (0.020 M) with *i*-PrCHO (0.13 M) in CH_2Cl_2 at –78 °C afforded adduct **6** at tractable rates. The absence of chelation in alkoxide **6** was shown by carbonyl absorbances that were nearly indistinguishable from those of starting oxazolidinone **1**. The absence of aggregation was

shown experimentally using MCV (*vide supra*) and supported by DFT computations predicting the dimerization of alkoxide **6** (eq 1.10) to be highly endothermic.[26]



(1.10)

Reactions under pseudo-first-order conditions (0.0050 M enolate **4** and 0.050 M *i*-PrCHO) showed first-order decays of enolate and k_{obsd} that were independent of the initial enolate concentration (Figure 1.5). The rate was unaffected by excess Et_3N or added tetrahydrofuran. The rate law in eq 11 is consistent with a simple aldol addition mechanistically akin to that proposed by Evans in the original work (**5** in Scheme 1.1). DFT studies mirroring those reported by Kobayashi and co-workers[6] showed transition structure **5a** to be both viable and 4.7 kcal/mol more stable than transition structure **5b** leading to the wrong isomer.[1,2]

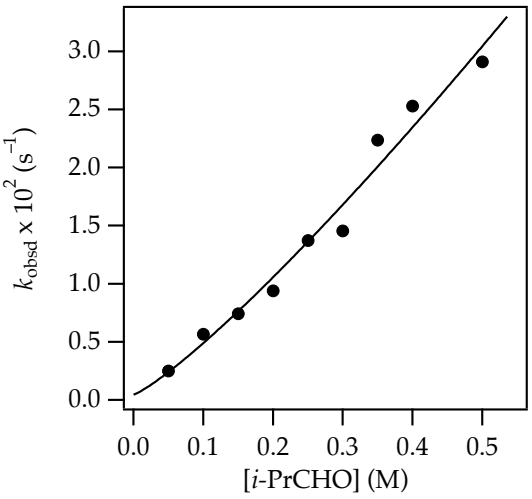
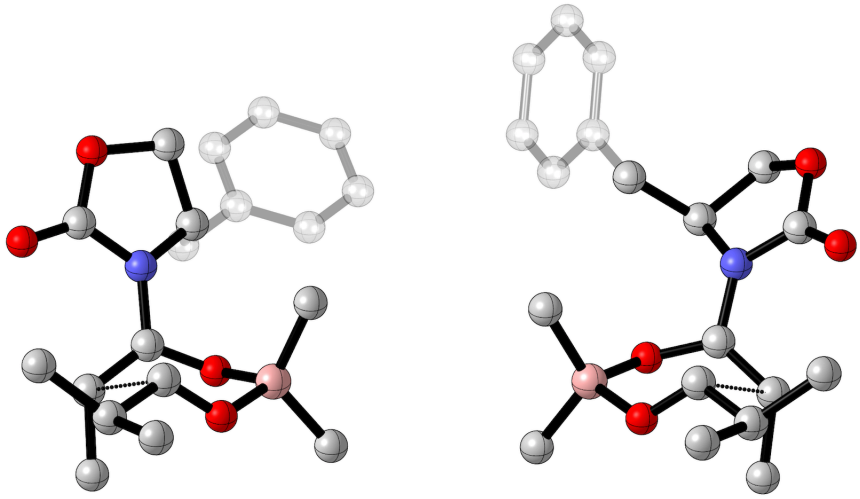


Figure 1.5. Plot of k_{obsd} versus *i*-PrCHO concentration for aldol addition by enolate **4** (0.0050 M) with a slight (0.0010 M) excess of Et_3N in $CHCl_3$ at –60 °C. $y = ax^b$, a = 0.067 ± 0.007, b = 1.09 ± 0.10.

$$-d[\mathbf{4}]/dt = k'[\mathbf{4}][i\text{-PrCHO}] \qquad (1.11)$$



5a **5b**

Discussion

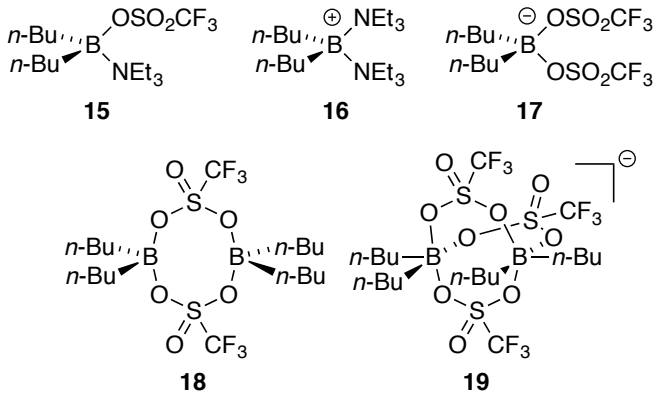
The structural and mechanistic studies of the Evans boron aldol addition proceeded largely according to conventional wisdom. Treating oxazolidinone **1** at 20 °C with *n*-Bu_2BOTf causes the instantaneous formation of complex **3**. Full complexation requires cooling to –60 °C or the use of excess *n*-Bu_2BOTf at 20 °C. Treatment of **3** with trialkylamines at –78 °C effects instantaneous enolization to give boron enolate **4**. Aldol addition to *i*-PrCHO at –60 °C affords boron alkoxide **6**.

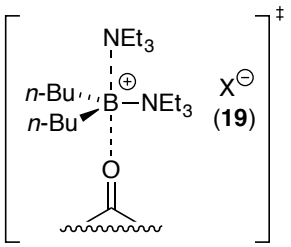
IR spectroscopy provided compelling support for the chelates in **3** and **4**, whereas the carbonyl of **6** does not coordinate to boron. Computations were in full accord with the monomeric alkoxide **6**.[26] MCV also provided no evidence that **3**, **4**, or **6** aggregate.

The high rates of complexation and enolization were overcome using *n*-$Bu_2BOTf{\cdot}Et_3N$ mixtures, which caused a marked attenuation of the complexation rate. The rate studies confirmed a rate-limiting complexation followed by rapid (post-rate-limiting) enolization. The success of the standard boron aldol addition stems from the fact that the incomplete **1**–**3** equilibrium is driven to enolate **4** by the enolization. Switching to *n*-$Bu_2BOTf{\cdot}$*i*-Bu_3N displaces the equilibrium toward observable complex **3** and shifts the rate-limiting step to proton transfer (Scheme 1.2).[23]

The details of the complexation are very odd. Although complex **3** represents a simple $CF_3SO_3^-$ ("X^-"), a third-order dependence on *n*-$Bu_2BOTf{\cdot}Et_3N$ in conjunction with an inverse-first-order dependence on amine implicates a rate-limiting transition structure with an unexpected $[(n\text{-}Bu_2BOTf)_3(Et_3N)_2(\mathbf{1})]^{\ddagger}$ stoichiometry.[25,27] Chart 1.2 shows a number of fragments—possible building blocks—that could be in play ranging from highly plausible to merely conceivable. The titration of *n*-Bu_2BOTf with Et_3N clearly shows a 1:1 complex consistent with **15**. A single *n*-Bu group excludes the ion pair of **16** and **17**. Dimer **18** is supported by limited literature precedent,[28] but it offers us nothing useful. The 3:2 stoichiometry demands a reactive form such as that composed of Lewis acidic **16** *and* counterion **19** with five-coordinate borons. The evidence of five-coordinate boron is sound[29]. We piece this together into to create transition structure **20** for rate-limiting complexation. The five-coordinate, trigonal bipyramidal substitution at boron has strong precedent from some rate studies we did a dozen years ago on imine activation by BF_3-R_3N complexes.[30] The complex genenion remains the controversial portion. And, as a referee noted, if the third-order dependence in Figure 3 is actually a second-order dependence that is in error—it happens—one can replace gegenion **19** with the far more conventional **17**. It would be an understatement to say that we are uneasy about parts of the model.

Chart 1.2. Possible boron-containing fragments.





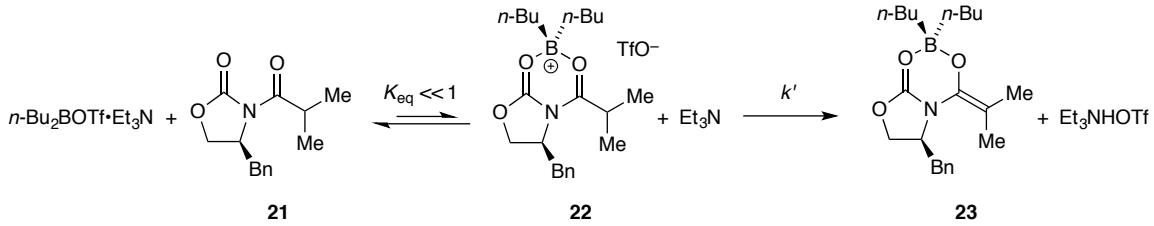
20

As an aside, the kinetics using the *n*-Bu_2BOTf·*i*-Pr_2NEt bearing a more hindered trialkylamine to form enolate **4** shows a 30-fold acceleration relative to the kinetics with the Et_3N variant, as expected for a mechanism requiring an amine dissociation. Interestingly, the measured reaction order in *n*-Bu_2BOTf·*i*-Pr_2NEt approaches unity (n = 1.3). The complex counterion may be unfavorable if the cation fragment (analogous to **16**) becomes too congested.

The final step—the aldol addition of **4** to give **6** via transition structure **5** (Scheme 1)—is mechanistically uneventful. Neither Et_3N nor added tetrahydrofuran inhibits the reaction, which shows that the putative four-coordinate boron in **4** is undisturbed by Lewis basic ligands. Kobayashi and co-workers[6] carried out calculations probing the nuances of **5** and competing orientations. These reactions showed consistency in the open transition structure and approach of the aldehyde anti to the benzyl group.

Conclusion

We described studies of the boron enolate-based Evans aldol addition. The most surprising aspect proves to be the mechanism of complexation, in which we may have uncovered some unusual organoboron coordination chemistry. The potentially most useful part, however, is probably the insights gained about the dual role of trialkylamines as inhibitors—complexants to the Lewis acid—and Bronsted bases. Suspecting that we could use this information to optimize the quaternization of the a-carbon using boron enolates,[4] we formed complex **22** from isobutyryl derivative **21**. The addition of Et_3N pushes the equilibrium to **21** rather than enolate **23**, however. More hindered trialkylamines promote complexation but are too unreactive as Brønsted bases. Thus, the quaternization faces challenges posed by such soft enolization methods.



It seems generally useful, even advisable, to understand the structural and mechanistic principles underlying synthetically prevalent reactions such as the Evans aldol addition.

Experimental

Reagents and Solvents. CH_2Cl_2, $CHCl_3$, and $CDCl_3$ were distilled from molecular sieves. Trialkylamines were distilled from sodium benzophenone ketyl. *n*-Bu_2BOTf was used as a neat oil by evaporating the solvent from a commercial 1.0 M *n*-Bu_2BOTf solution in CH_2Cl_2. Air- and moisture-sensitive materials were manipulated under argon using standard glovebox, vacuum line, and syringe techniques. Oxazolidinones **1** and **7**–**11** were either purchased or prepared as described previously.[31]

NMR Spectroscopy. An NMR tube under vacuum was flame-dried on a Schlenk line and allowed to return to room temperature, backfilled with argon, and placed in a –78 °C dry ice/acetone bath. The appropriate amounts of *n*-Bu_2BOTf, Et_3N, and oxazolidinone in $CDCl_3$ were added sequentially via syringe. The tube was flame-sealed under partial vacuum, mixed on a vortex mixer three times for ~10 s with cooling between each vortexing, and stored in a freezer at –80 °C. Standard ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a 500 MHz spectrometer at 500, 125, and 470 MHz, respectively. The ^1H, ^{13}C, and ^{19}F resonances are referenced to $CDCl_3$ ($CHCl_3$ 7.26 and $CDCl_3$ 77.16 ppm) and fluorobenzene (–113.15 ppm).

IR spectroscopic analyses. IR spectra were recorded with an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired in 16 scans at a gain of 1 and a resolution of 4 cm^{-1}. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was capped with a septum for injections and a nitrogen line. After evacuation under full

vacuum, heating, and flushing with nitrogen, the flask was charged with $CHCl_3$ and cooled in a –60 °C bath prepared with fresh acetone. After a background spectrum was recorded, oxazolidinone **1** (23.3 mg, 0.10 mmol) was added as a 1.0 M solution in $CHCl_3$ with stirring, followed by neat *n*-Bu_2OTf (30.2 mg, 0.11 mmol), neat Et_3N (12.1 mg, 0.12 mmol), and *i*-PrCHO (9.4 mg, 0.13 mmol). IR spectra were recorded every 15 s with monitoring of the absorbance at 1777 cm^{-1} and 1658 cm^{-1} over the course of the reaction.

CHAPTER 1 APPENDIX

Chapter 1 Appendix Table of Contents

1. IR Spectra

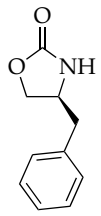
2. MCV Study

7. ^{11}B NMR Spectra

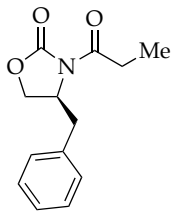
8. ^{19}F NMR Spectra

9. 1-d_1 Synthesis

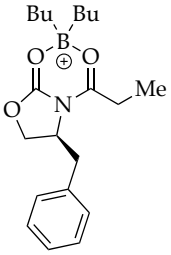
10. Computation Study



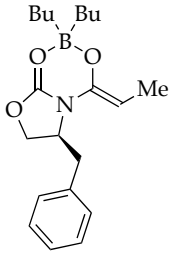
1S



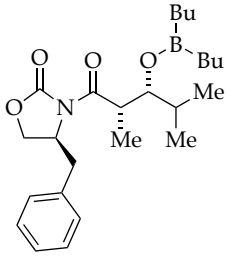
1



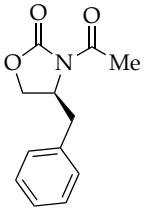
3



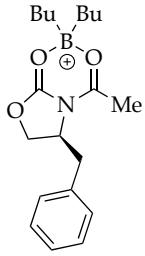
4



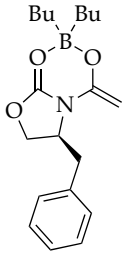
6



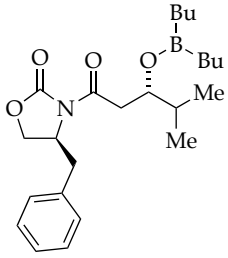
7



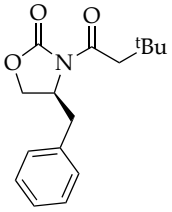
7a



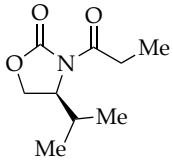
7b



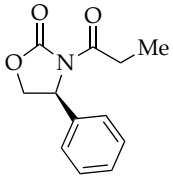
7c



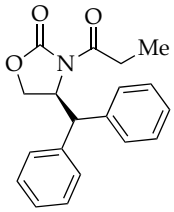
8



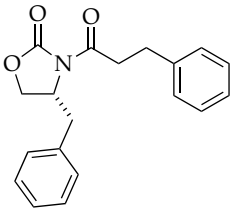
9



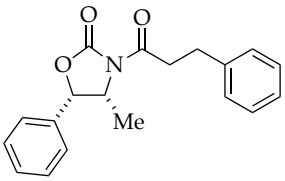
10



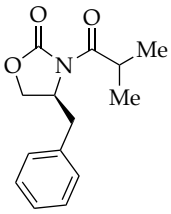
11



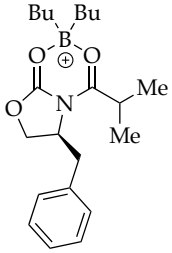
12



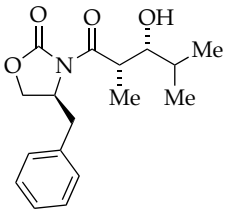
13



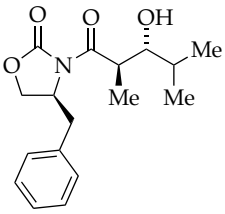
20



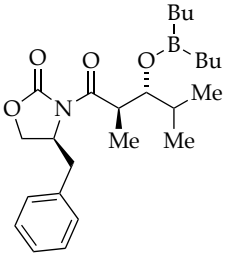
21



2



23



24

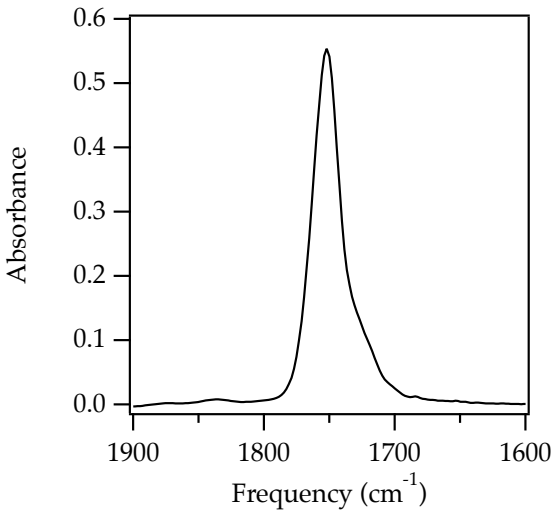


Figure A.1.1. IR spectrum of 0.30 M **1S** in $CHCl_3$ recorded at –60 °C.

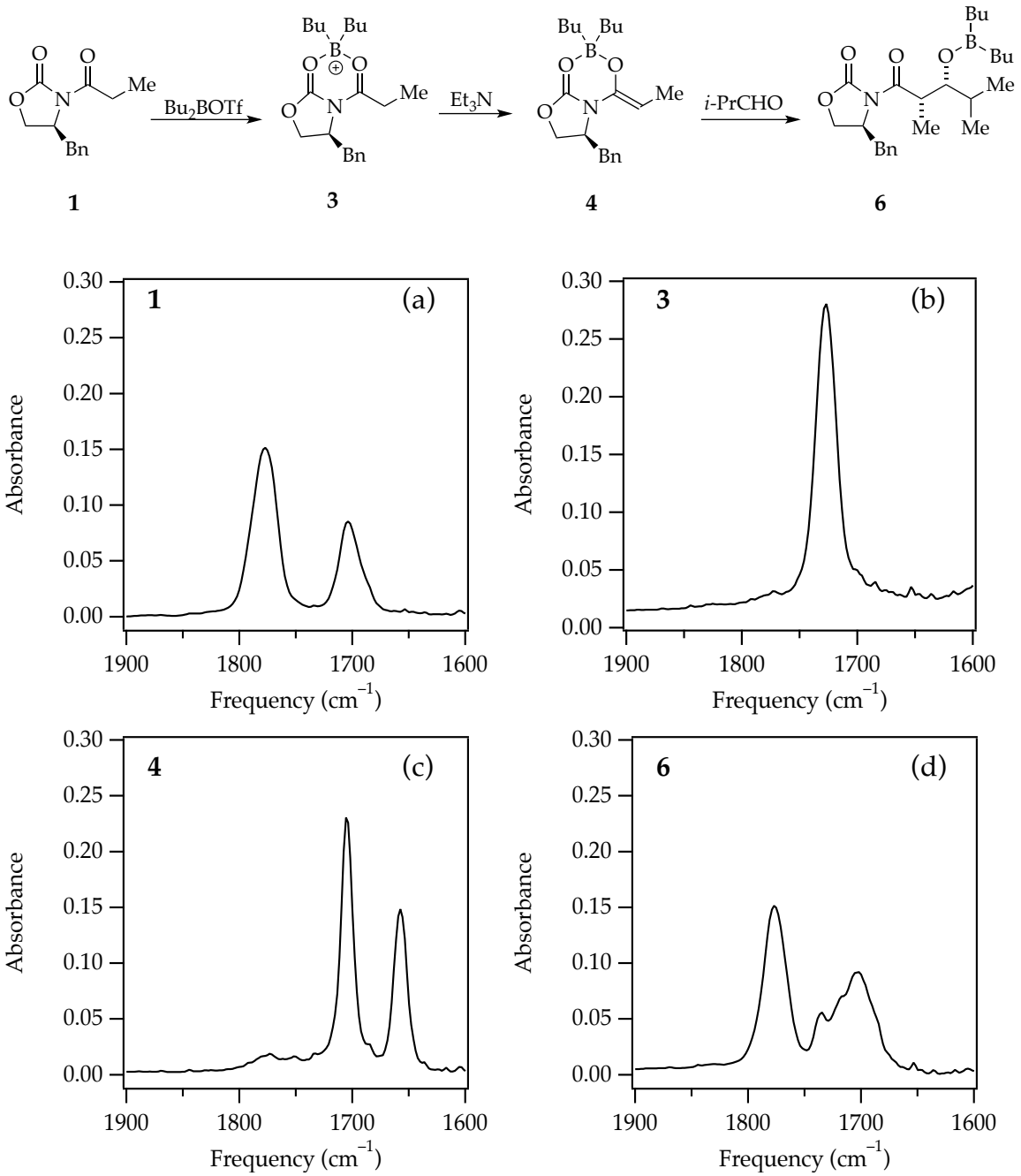
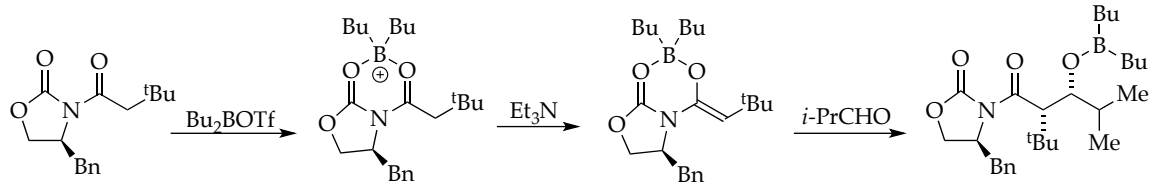
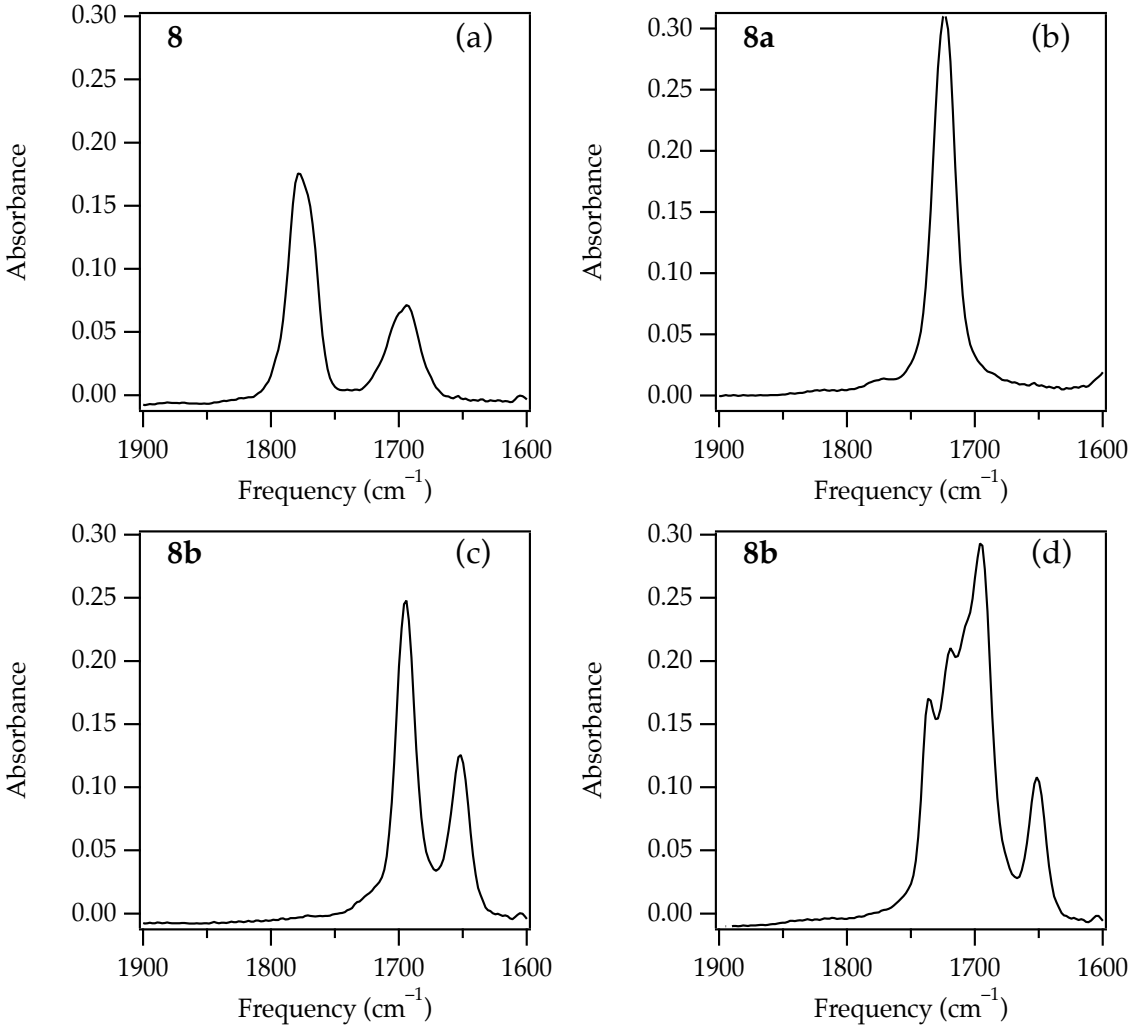


Figure A.1.2. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **1**; (b) 0.10 M **1** and 0.11 M Bu_2BOTf; (c) 0.10 M **1**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **1**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.


Bu2BOTf
Et3N
i-PrCHO
Bn
tBu
Me

8 **8a** **8b** **8c**


8
(a)
8a
(b)
8b
(c)
8b
(d)
Absorbance
Frequency (cm−1)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
1900
1800
1700
1600

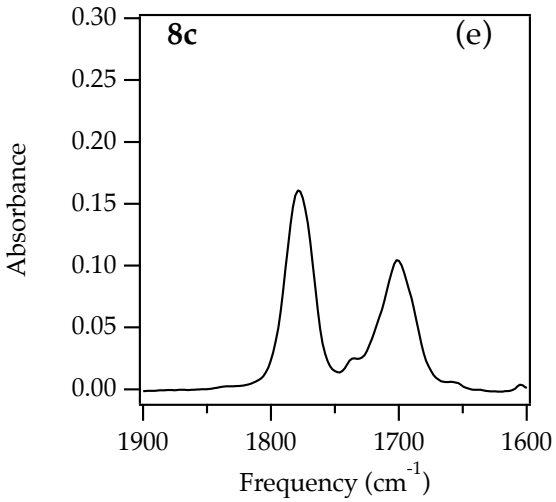


Figure A.1.3. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **8**; (b) 0.10 M **8** and 0.11 M Bu_2BOTf; (c) 0.10 M **8**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **8**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde; (e) 0.10 M **8**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde recorded at 0 °C.

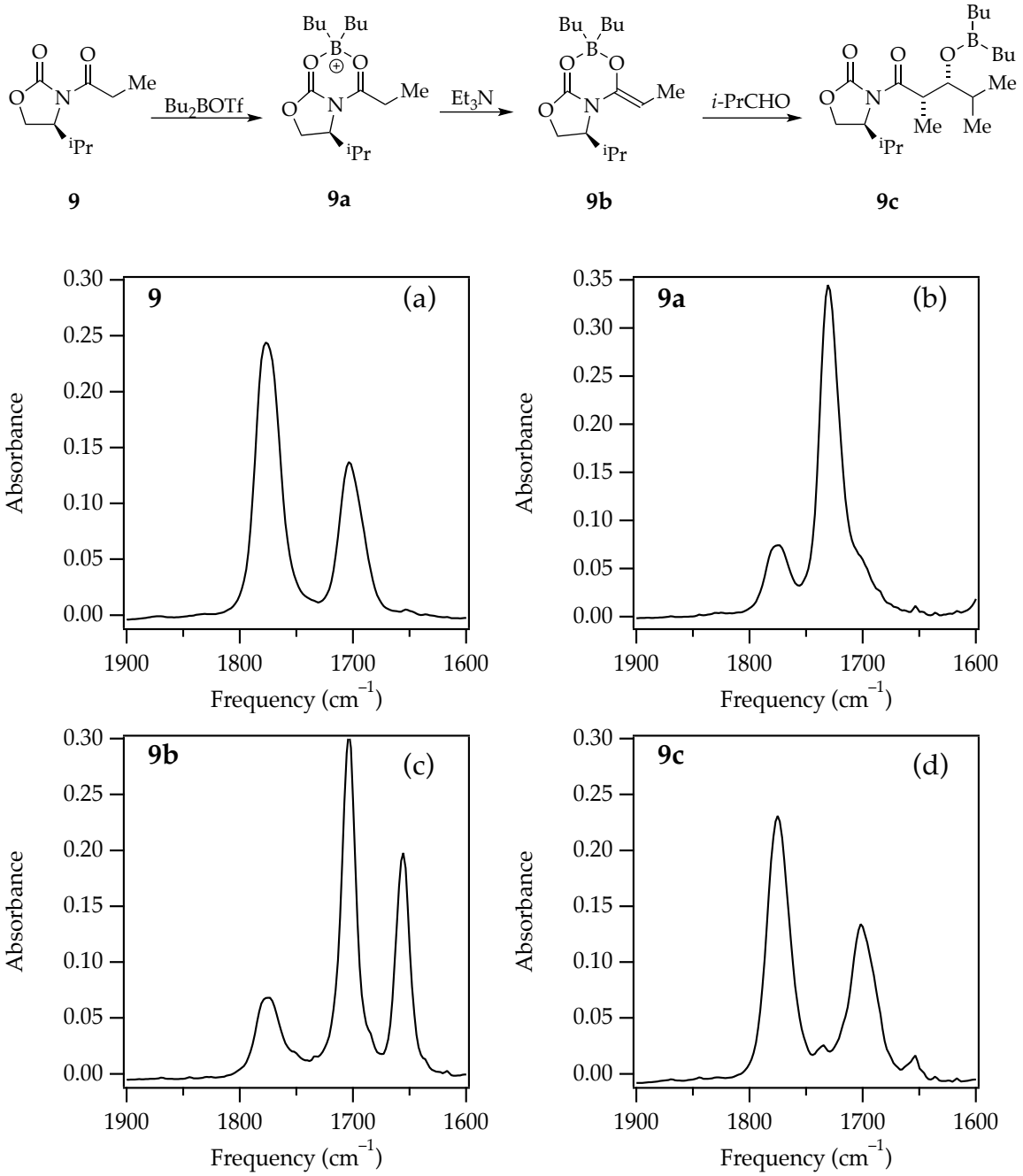


Figure A.1.4. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **9**; (b) 0.10 M **9** and 0.11 M Bu_2BOTf; (c) 0.10 M **9**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **9**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

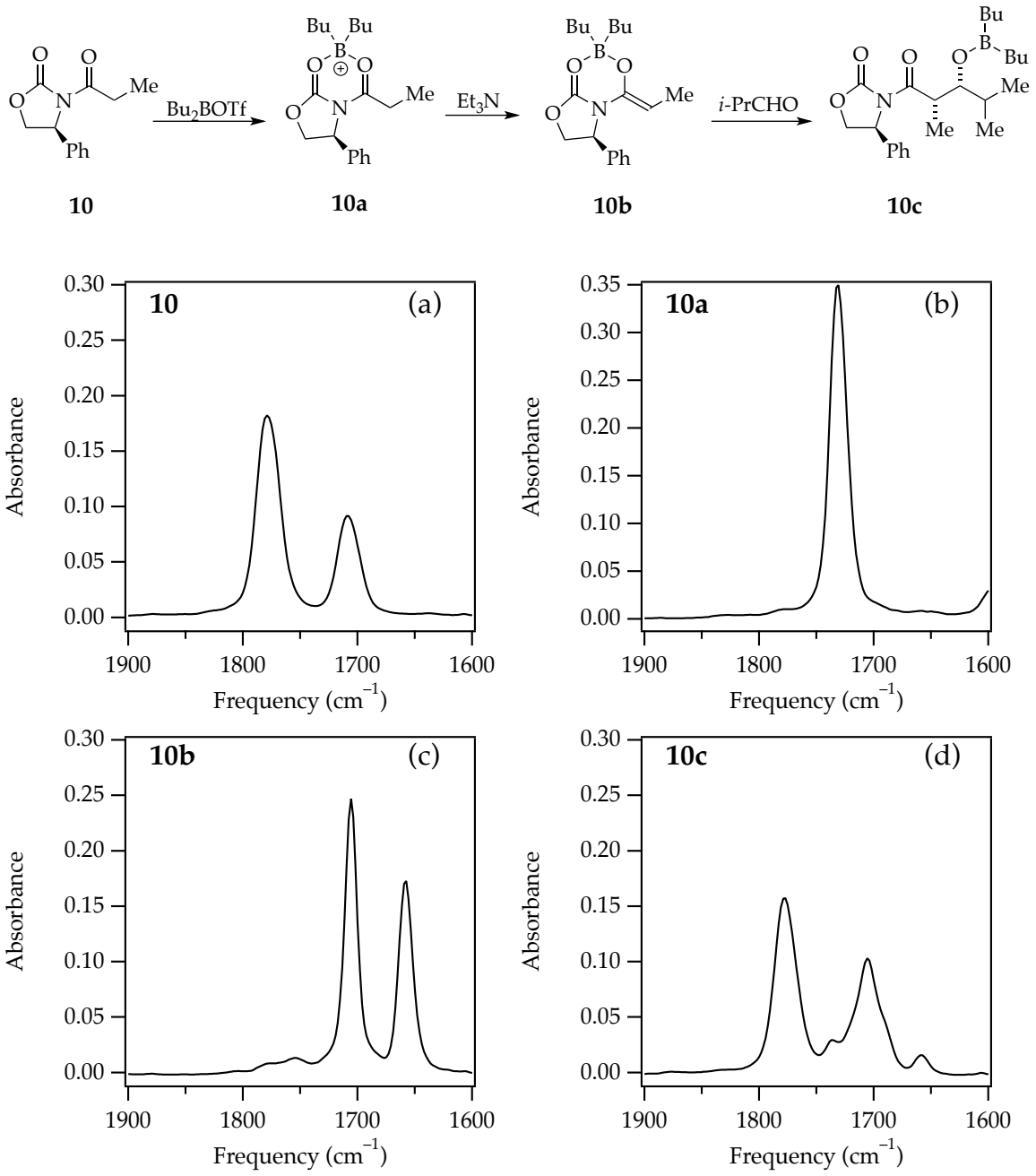


Figure A.1.5. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **10**; (b) 0.10 M **10** and 0.11 M Bu_2BOTf; (c) 0.10 M **10**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **10**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

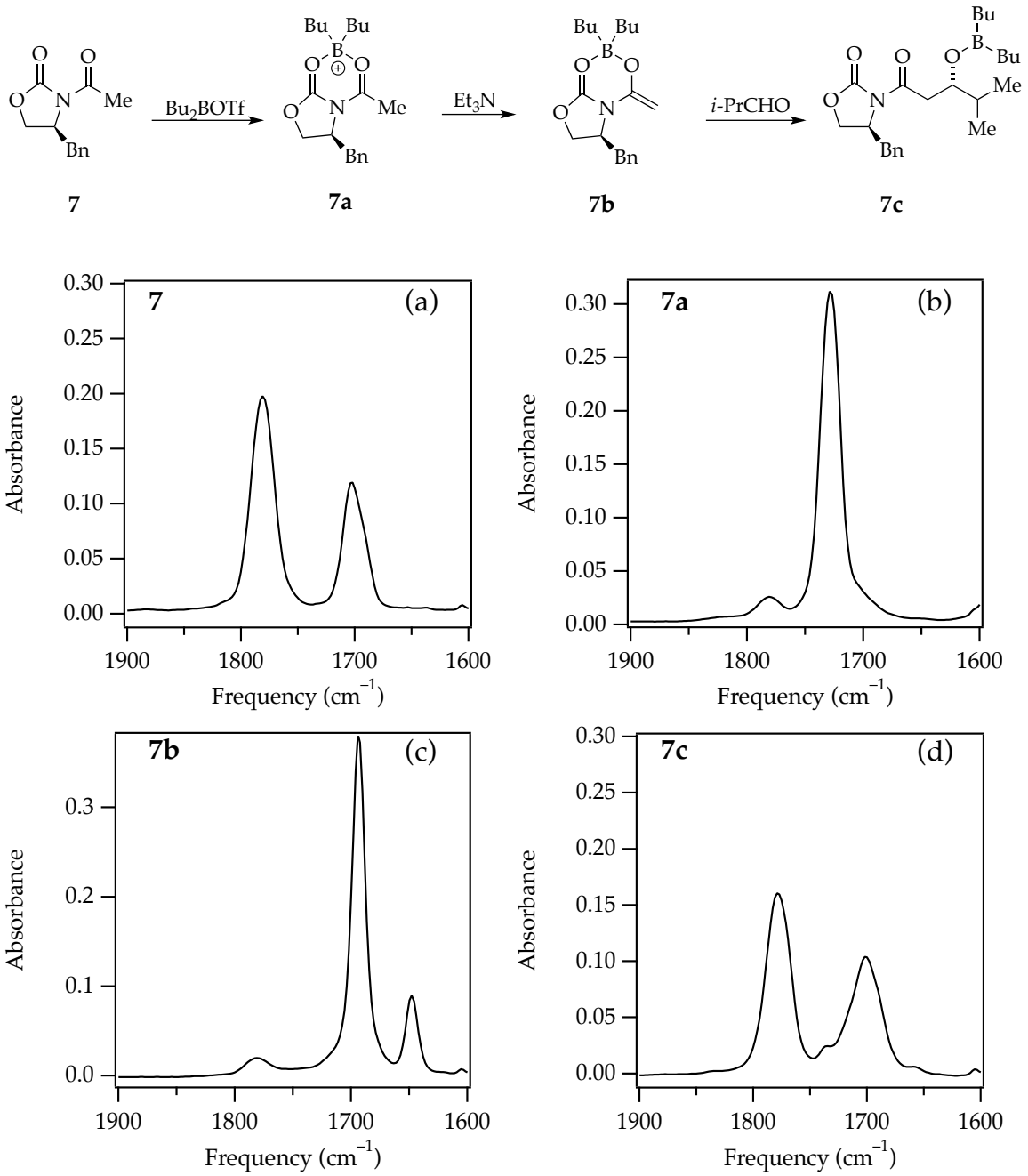


Figure A.1.6. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **7**; (b) 0.10 M **7** and 0.11 M Bu_2BOTf; (c) 0.10 M **7**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **7**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

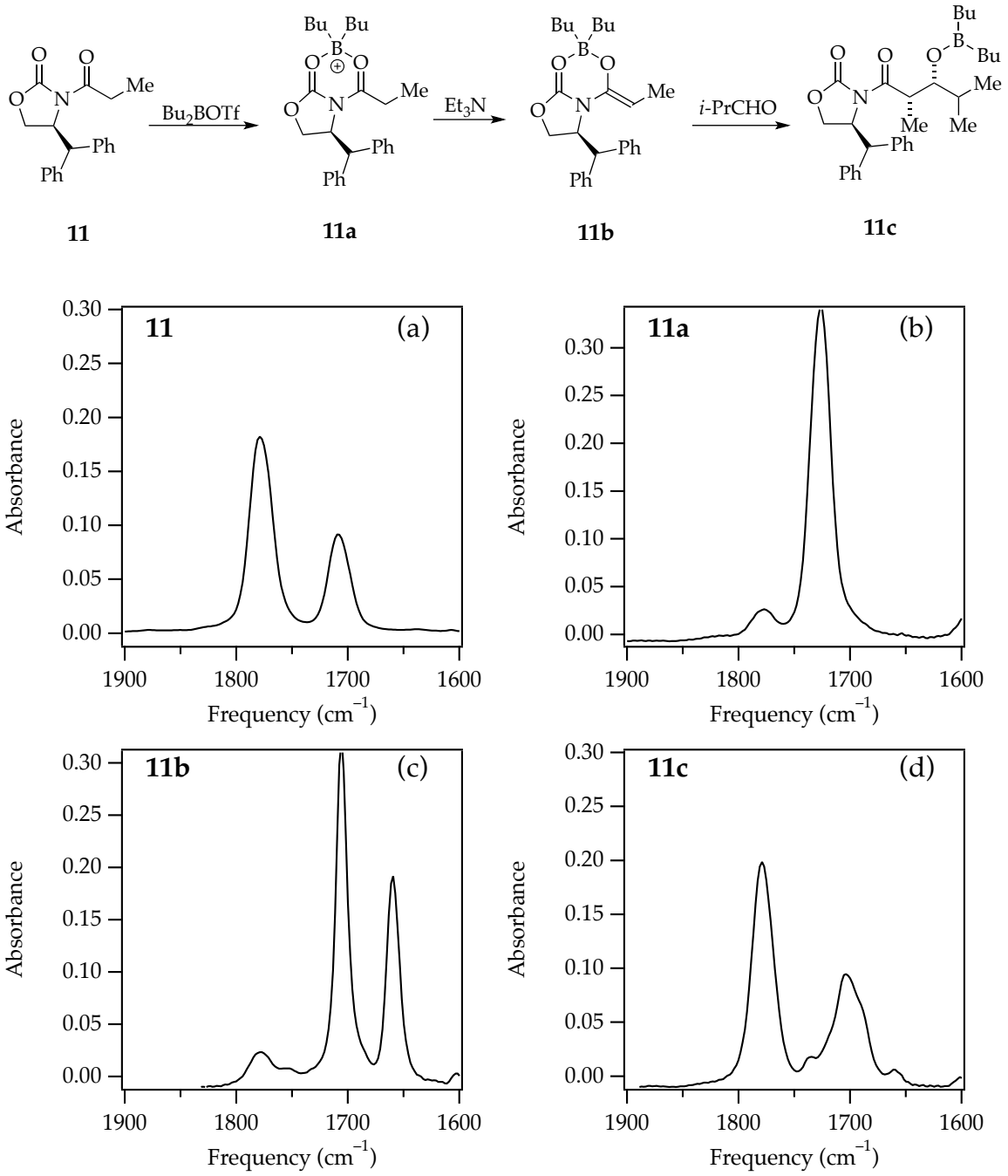


Figure A.1.7. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **11**; (b) 0.10 M **11** and 0.11 M Bu_2BOTf; (c) 0.10 M **11**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **11**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

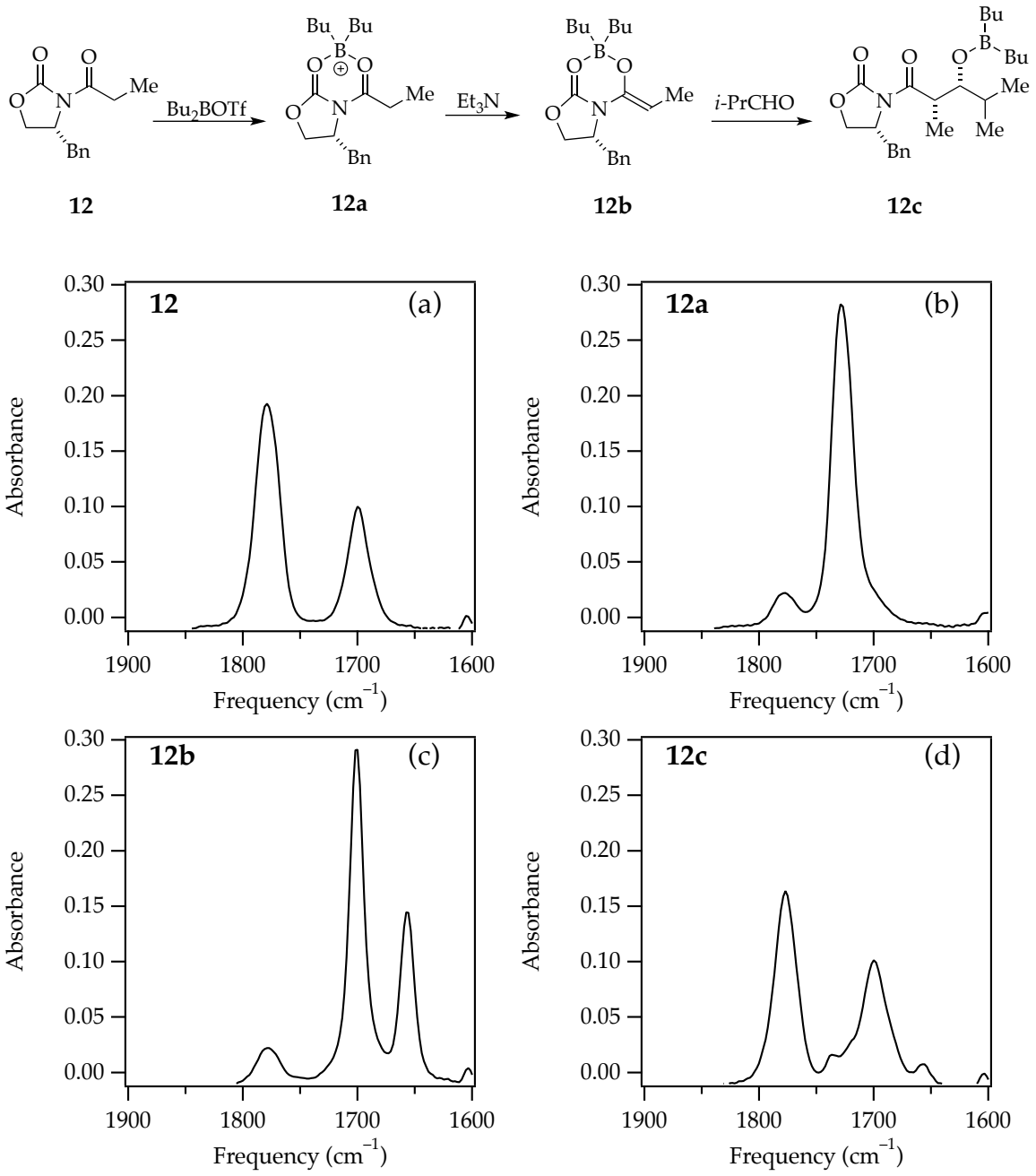


Figure A.1.8. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **12**; (b) 0.10 M **12** and 0.11 M Bu_2BOTf; (c) 0.10 M **12**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **12**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

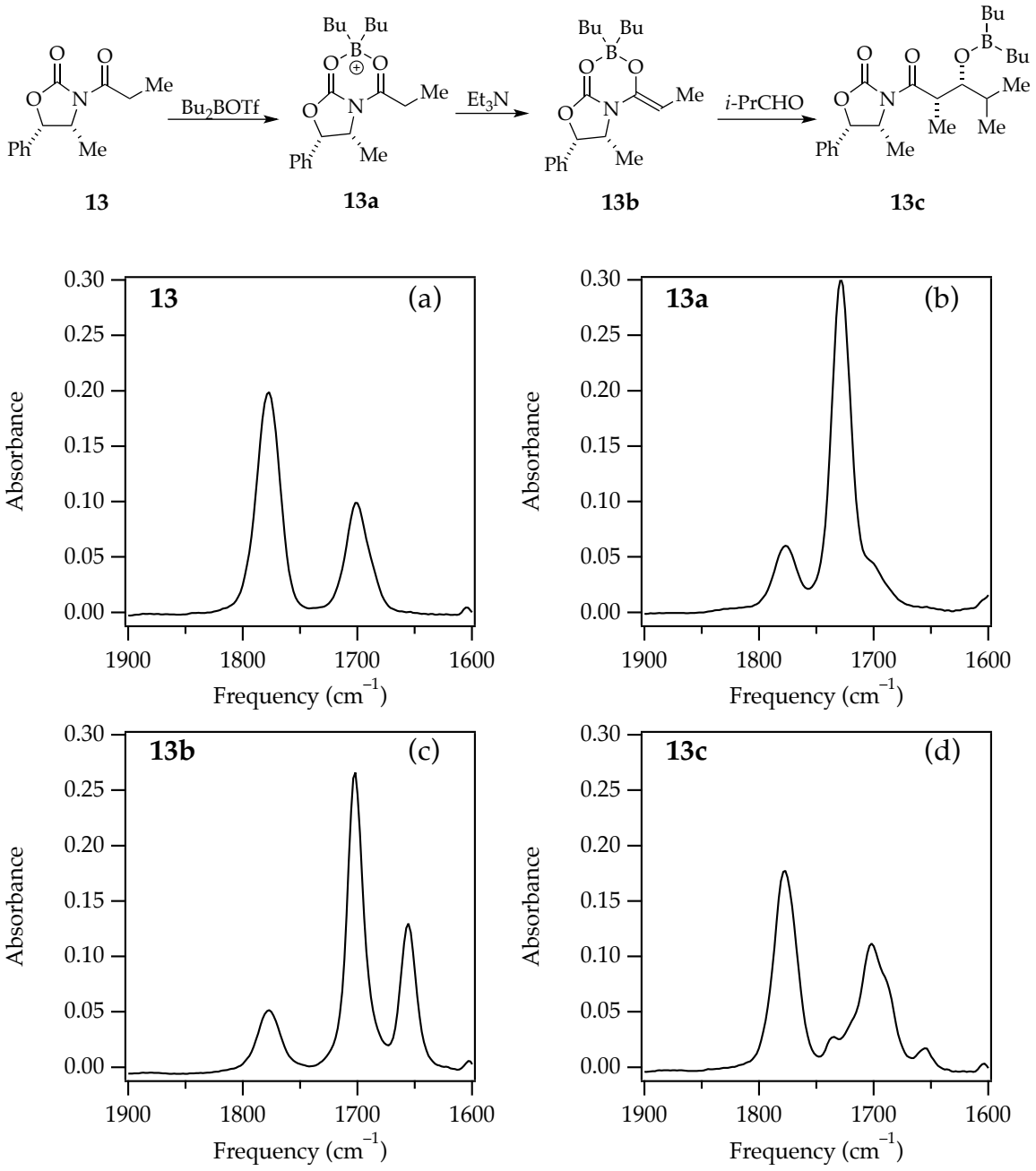


Figure A.1.9. IR spectra in $CHCl_3$ recorded at –60 °C: (a) 0.10 M **13**; (b) 0.10 M **13** and 0.11 M Bu_2BOTf; (c) 0.10 M **13**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (d) 0.10 M **13**, 0.11 M Bu_2BOTf, 0.12 M Et_3N, and 0.13 M isobutyraldehyde.

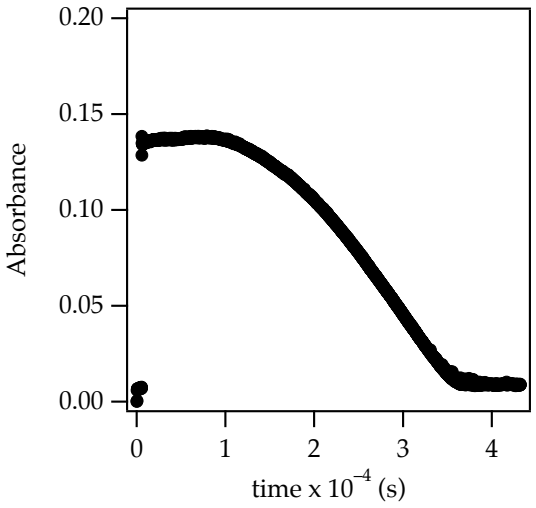


Figure A.1.10. IR spectra of 0.10 M **1**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N in $CHCl_3$ at rt, following decomposition of **4**.

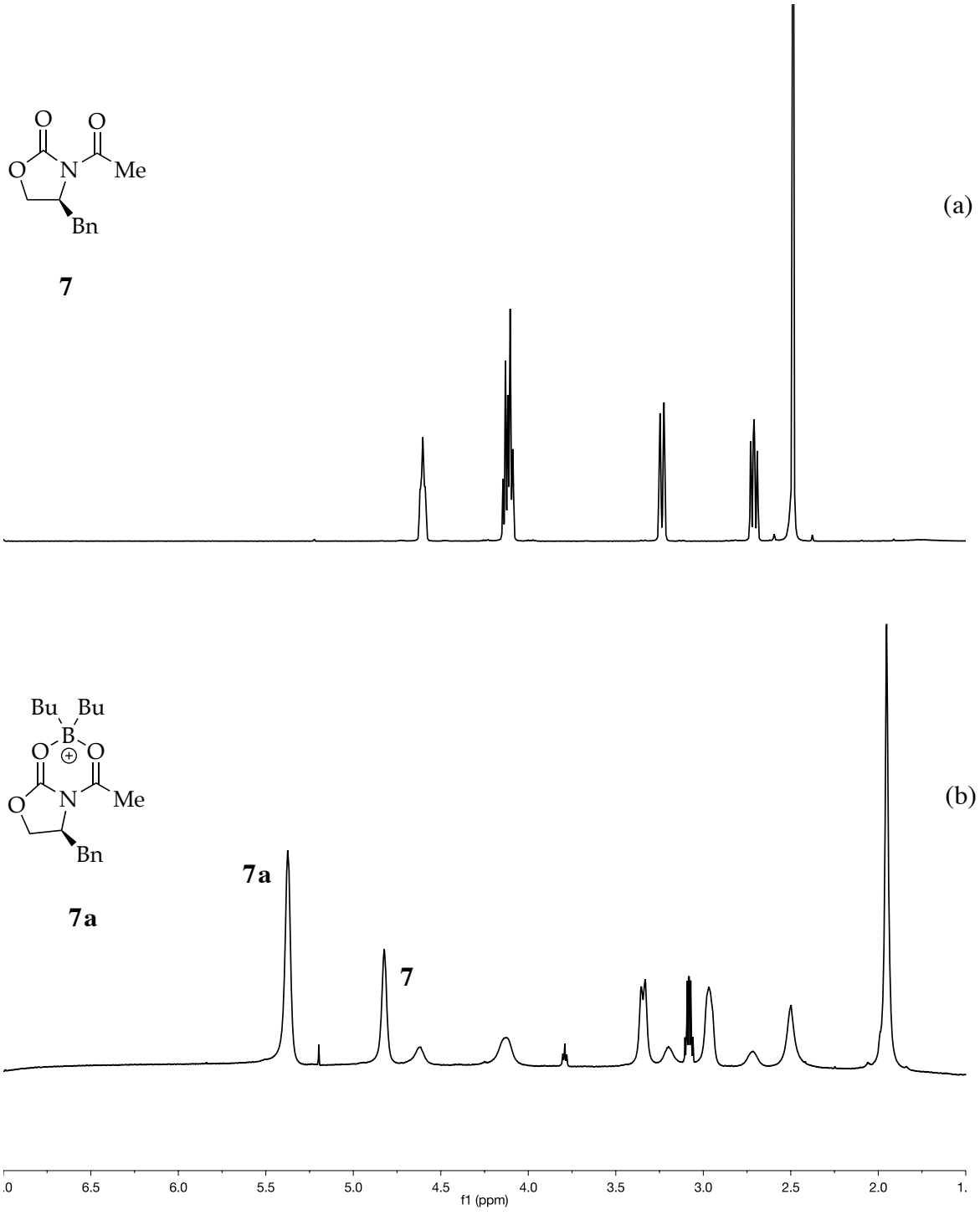


Figure A.1.11. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **7**; (b) 0.10 M **7** and 0.25 M Bu_2BOTf.

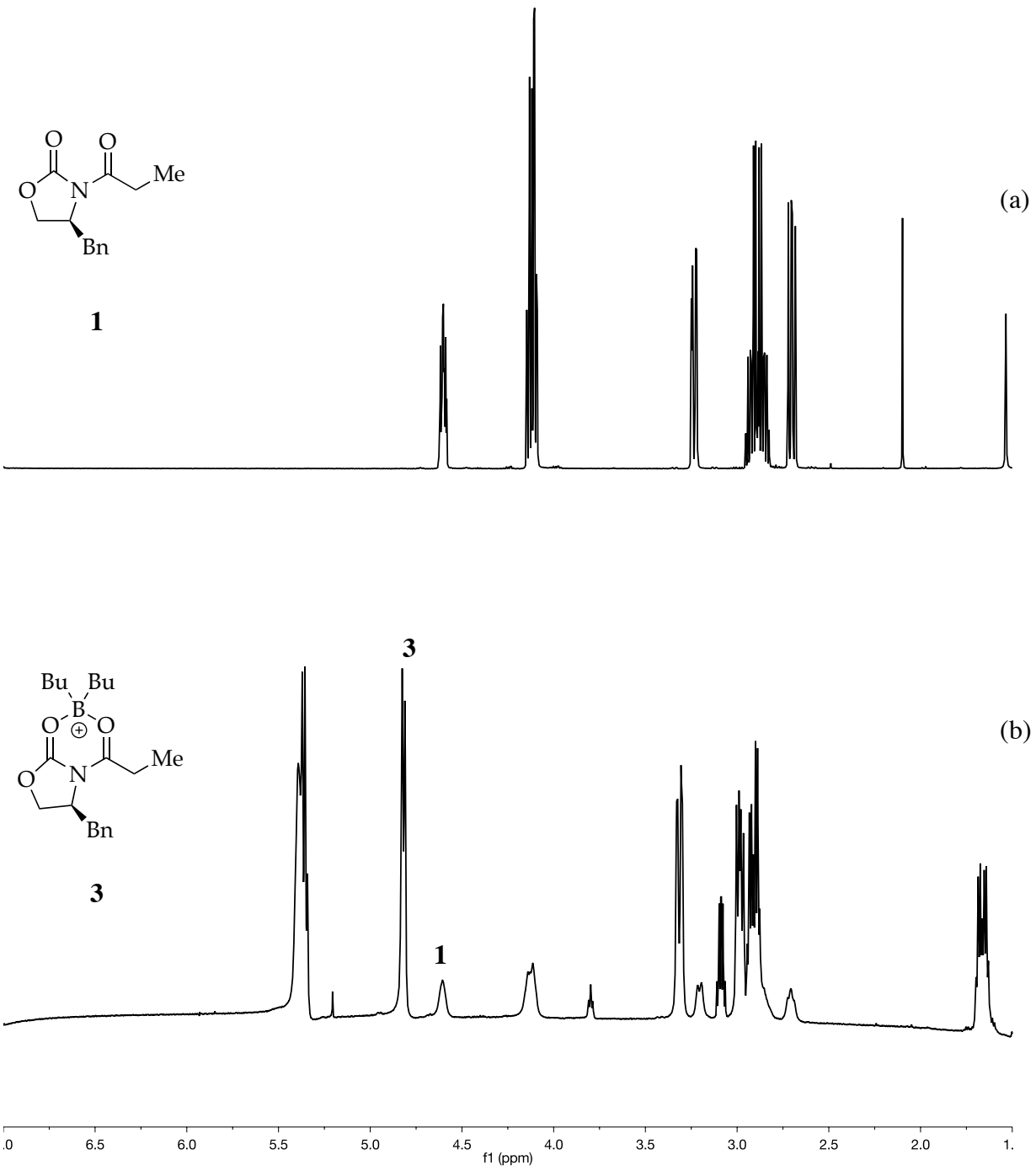


Figure A.1.12. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**; (b) 0.10 M **1** and 0.25 M Bu_2BOTf.

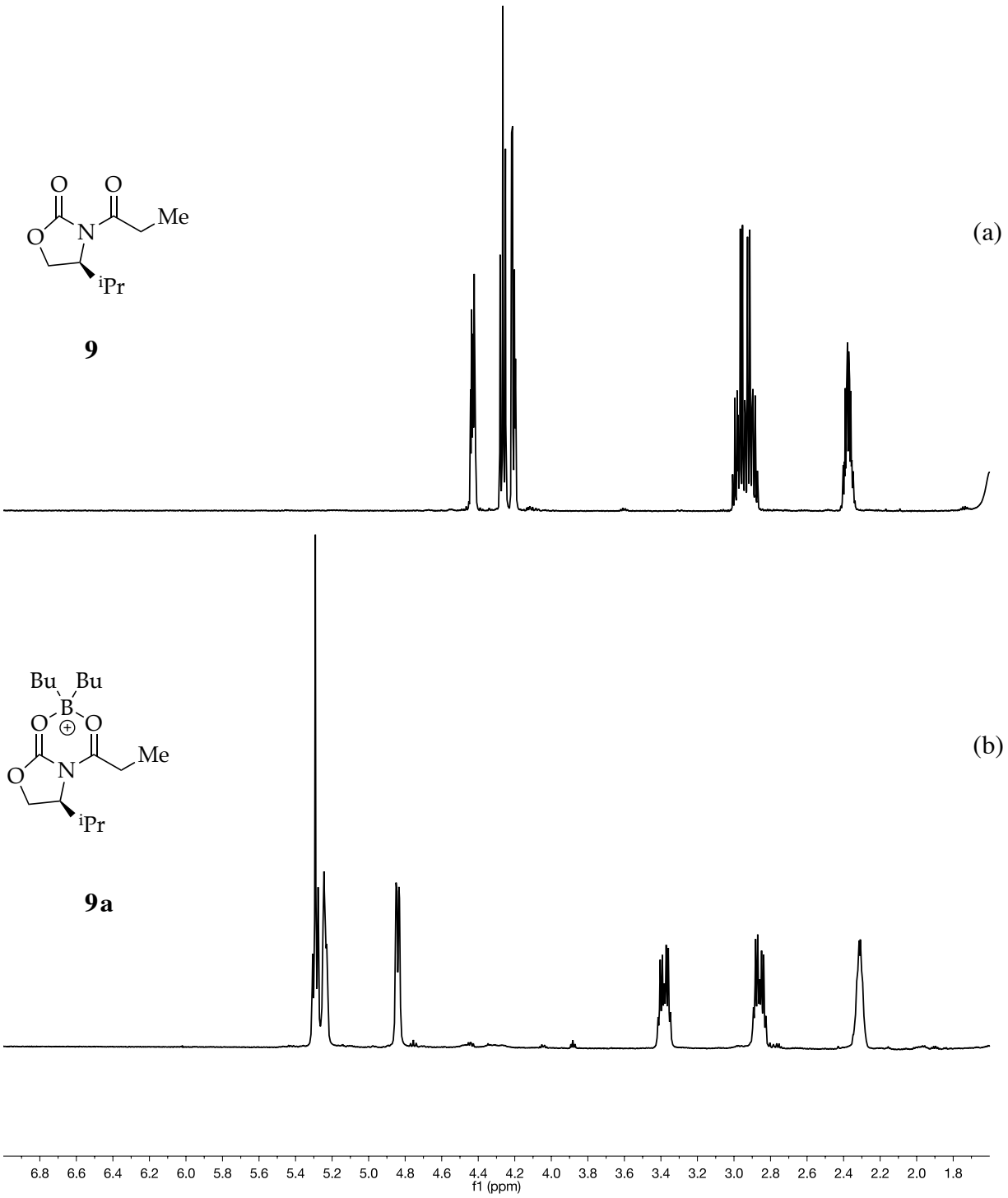


Figure A.1.13. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **9**; (b) 0.10 M **9** and 0.25 M Bu_2BOTf.

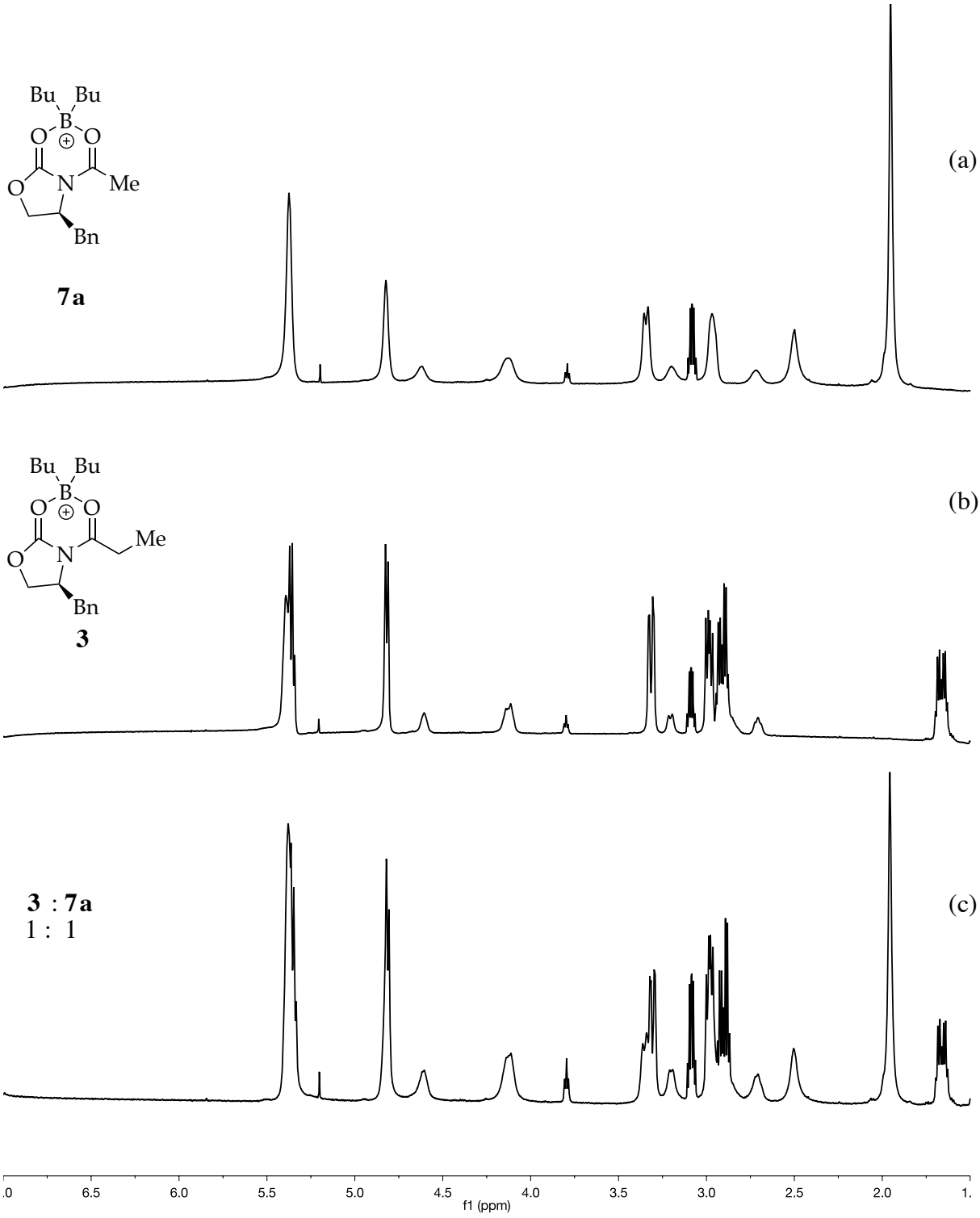


Figure A.1.14. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **7** and 0.25 M Bu_2BOTf; (b) 0.10 M **1** and 0.25 M Bu_2BOTf; (c) 0.050 M **7**, 0.050 M **1**, and 0.25 M Bu_2BOTf.

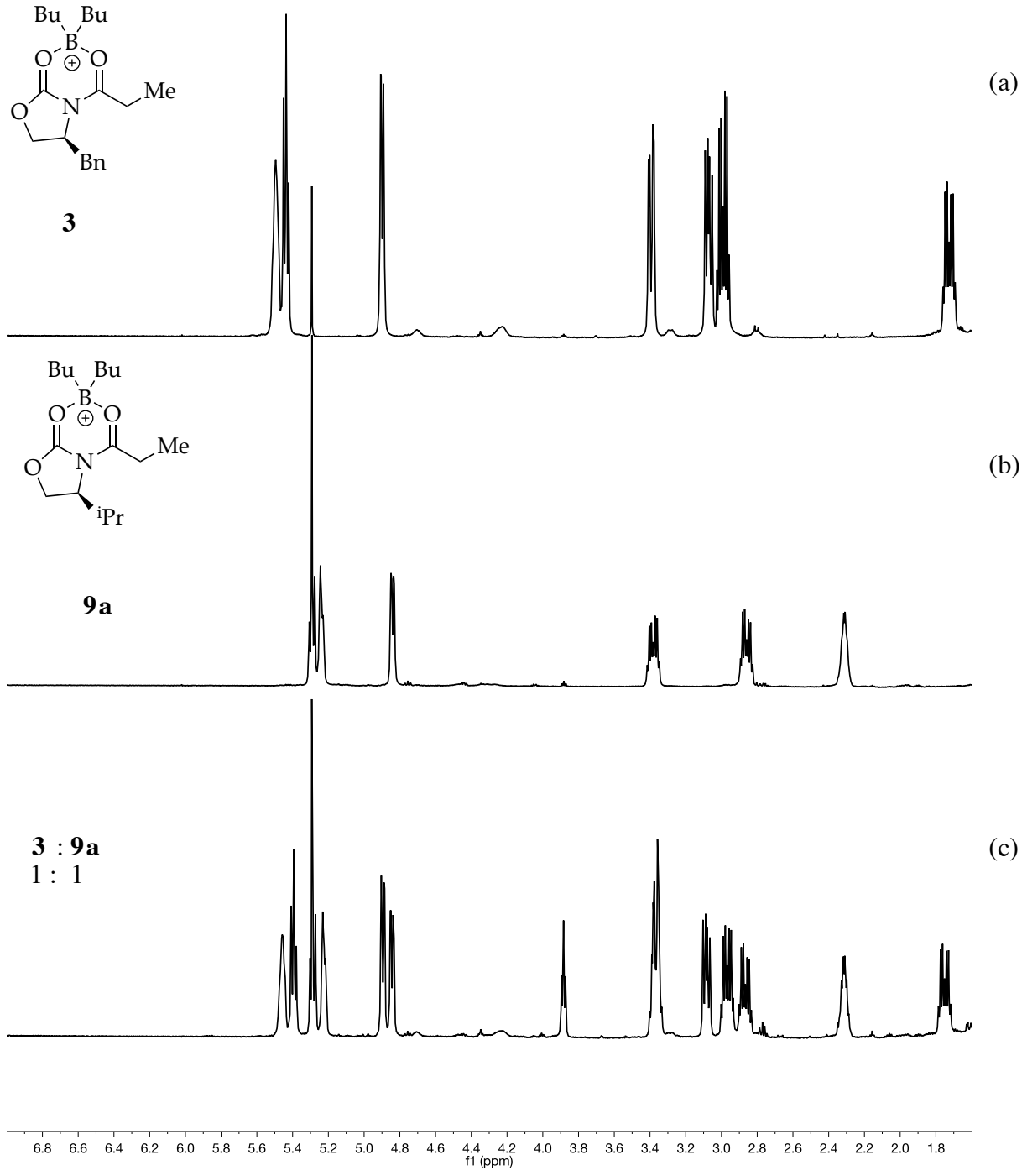


Figure A.1.15. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1** and 0.25 M Bu_2BOTf; (b) 0.10 M **9** and 0.25 M Bu_2BOTf; (c) 0.050 M **1**, 0.050 M **9**, and 0.25 M Bu_2BOTf.

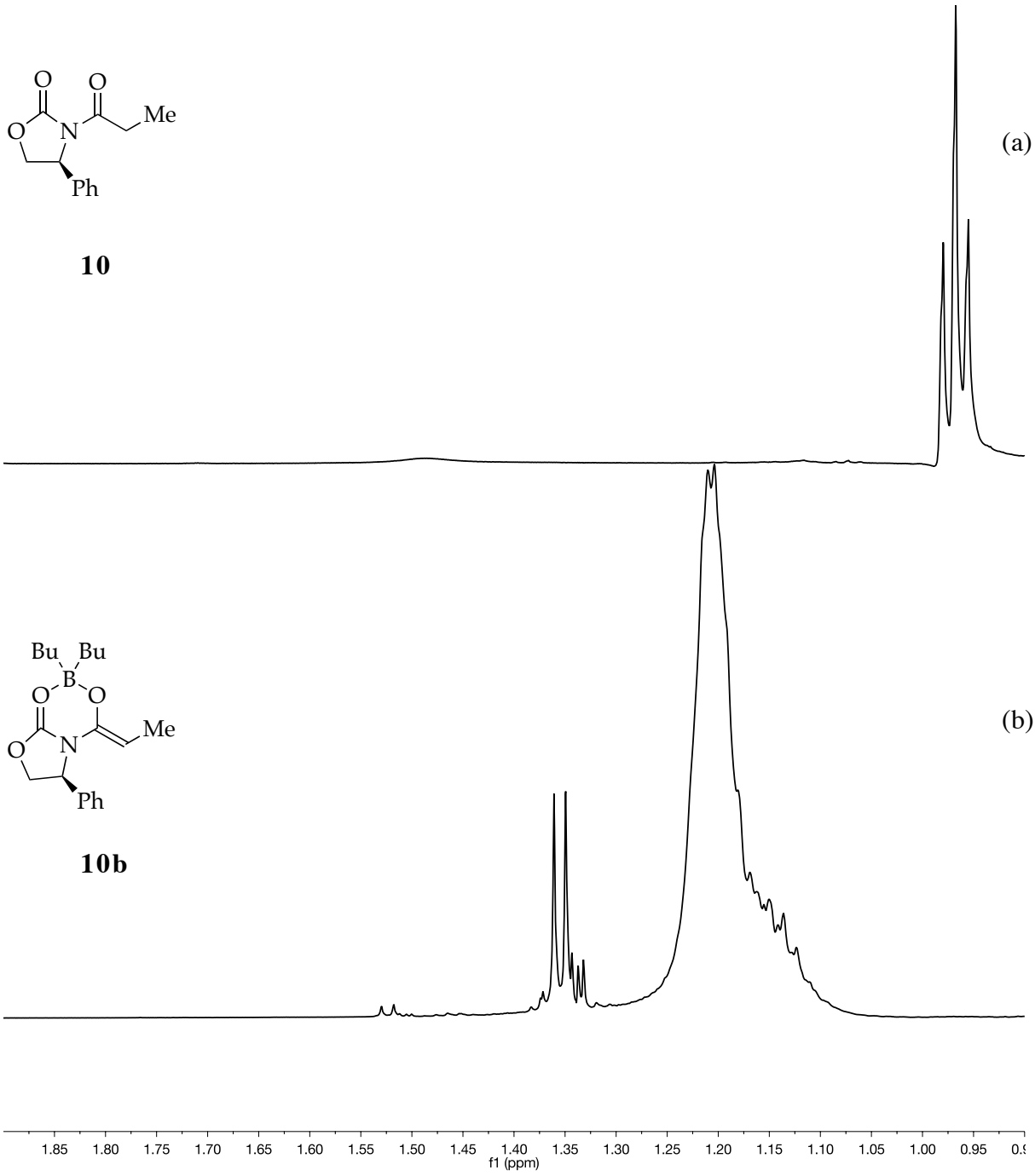


Figure A.1.16. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **10**; (b) 0.10 M **10**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

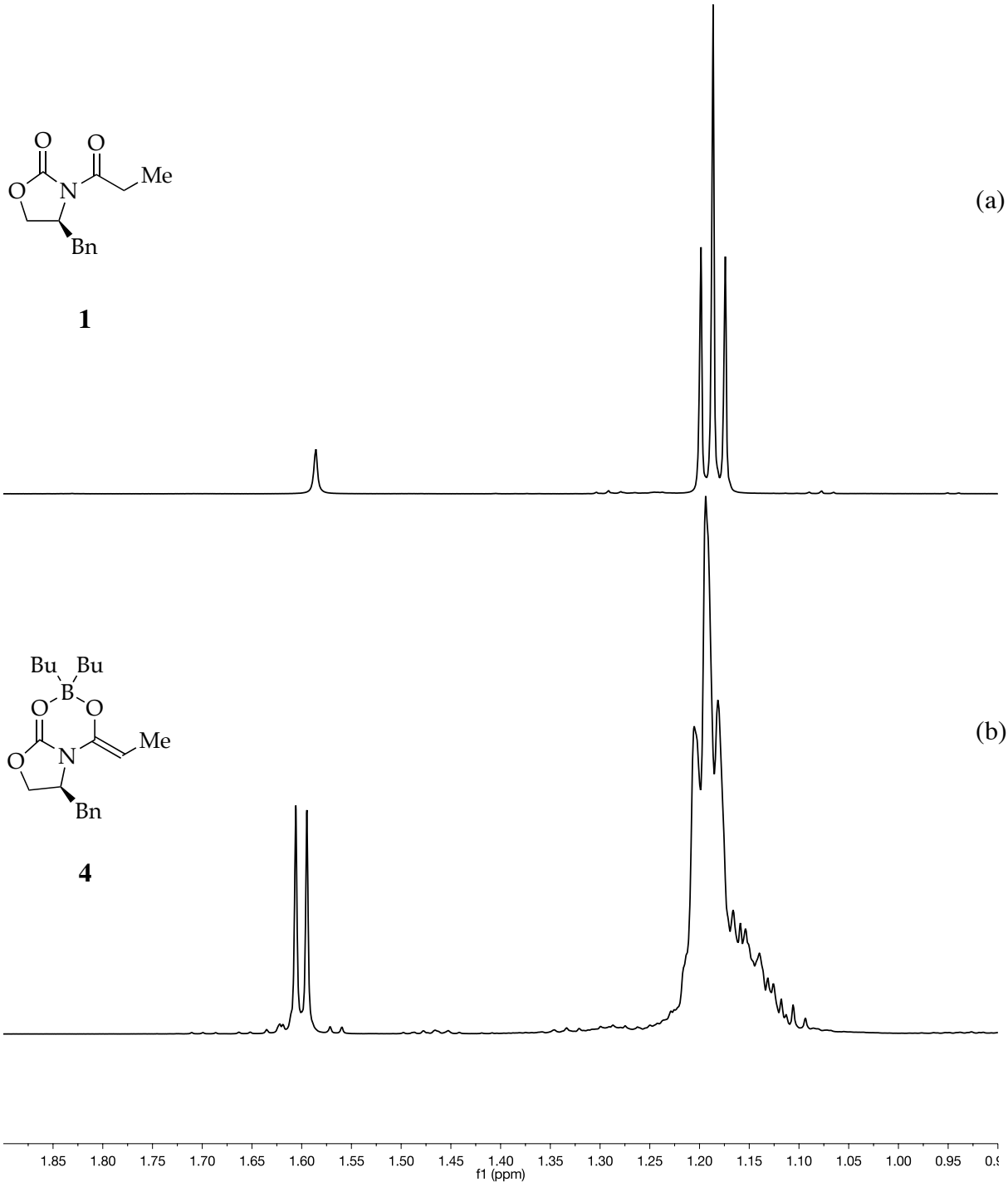


Figure A.1.17. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**; (b) 0.10 M **1**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

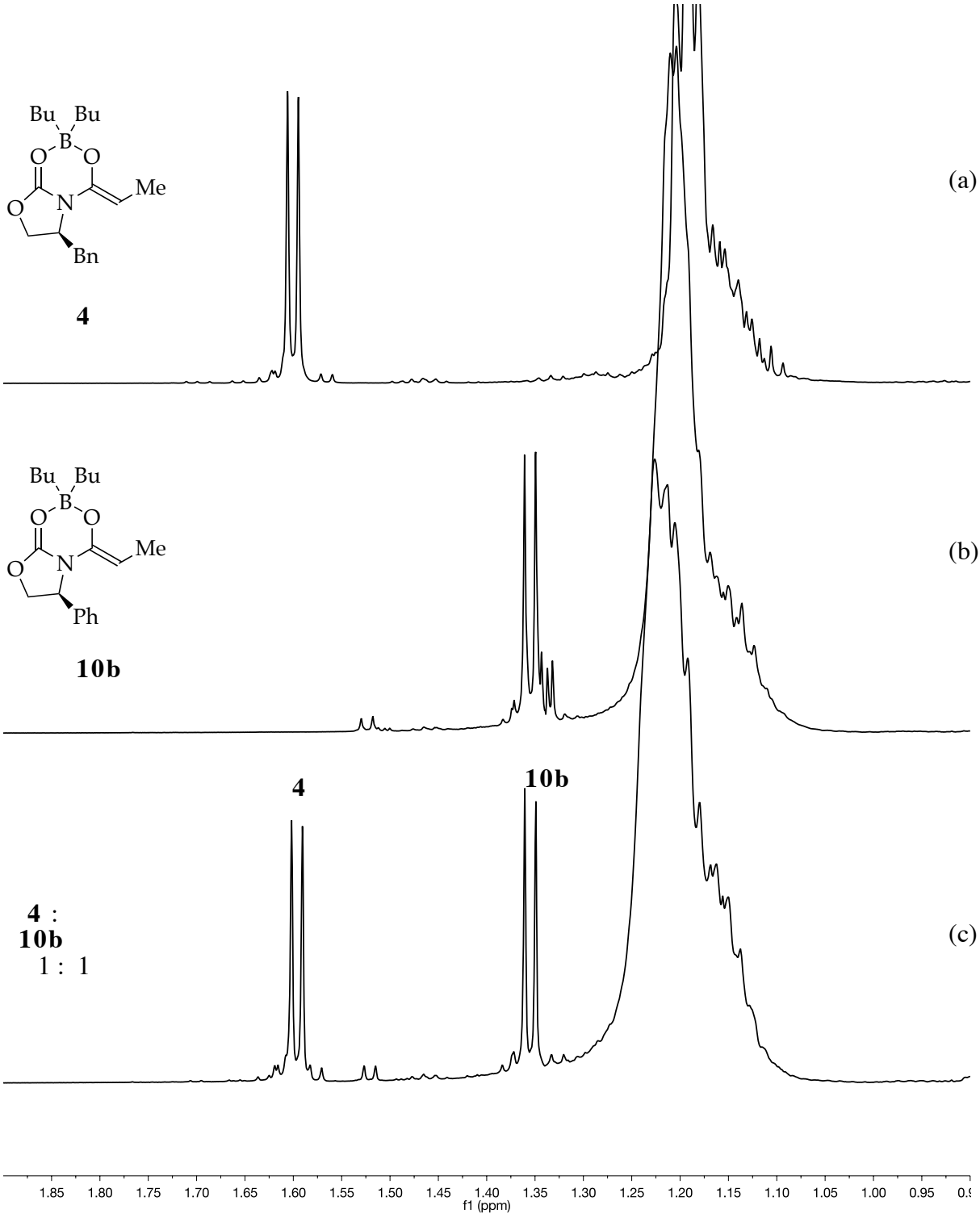


Figure A.1.18. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (b) 0.10 M **10**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (c) 0.050 M **1**, 0.050 M **10**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

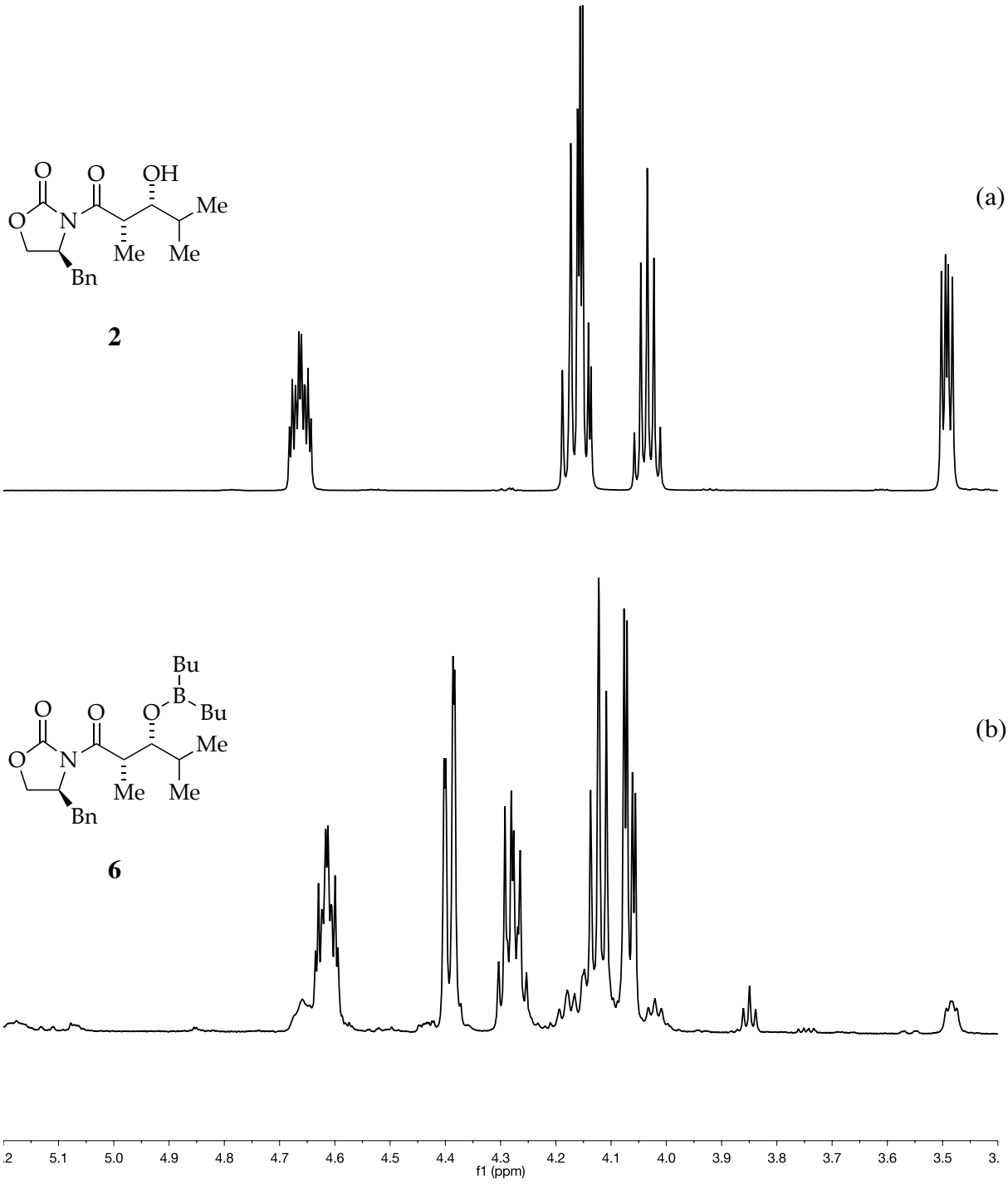


Figure A.1.19. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **2**; (b) 0.10 M **2**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

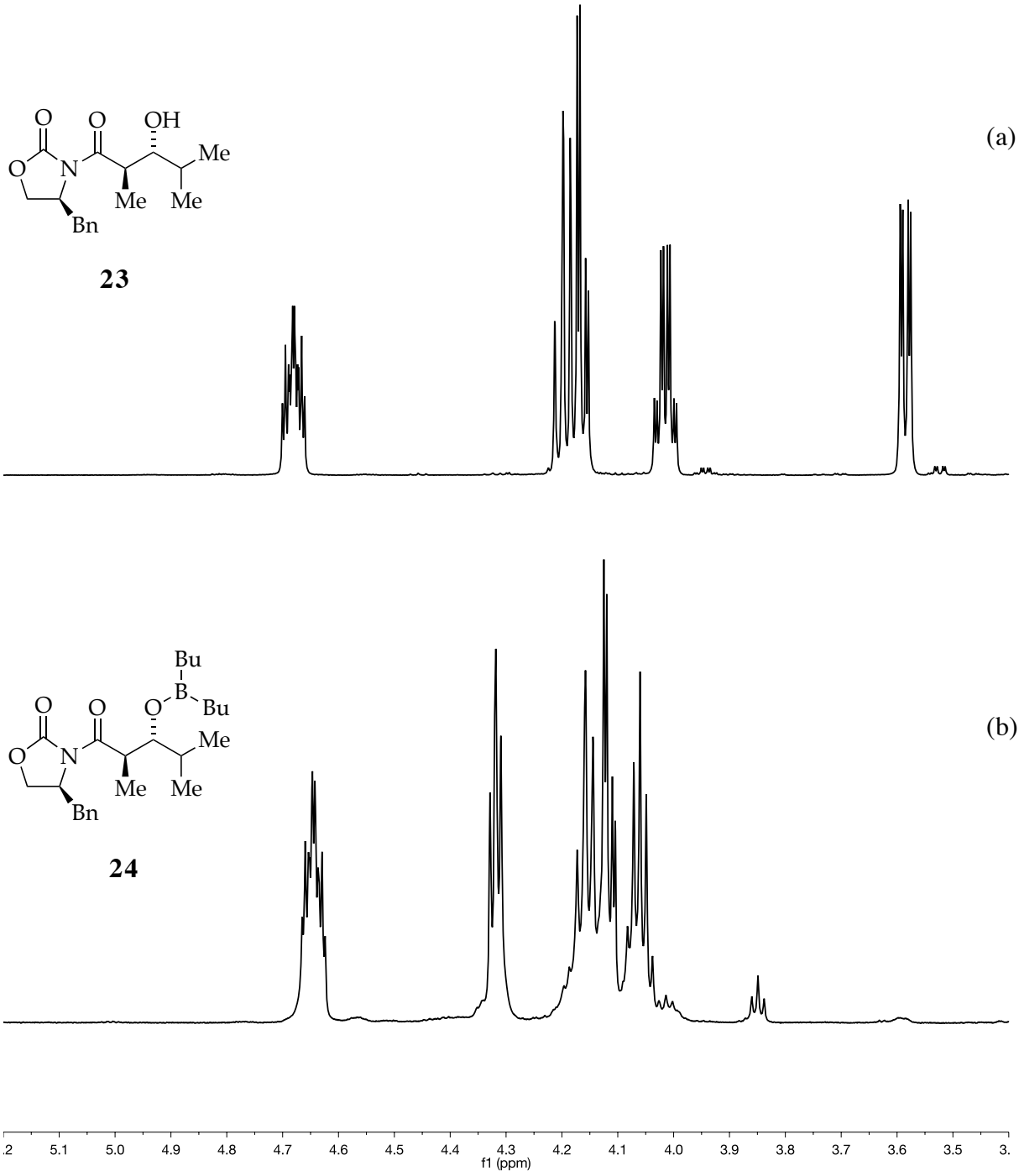


Figure A.1.20. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **23**; (b) 0.10 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

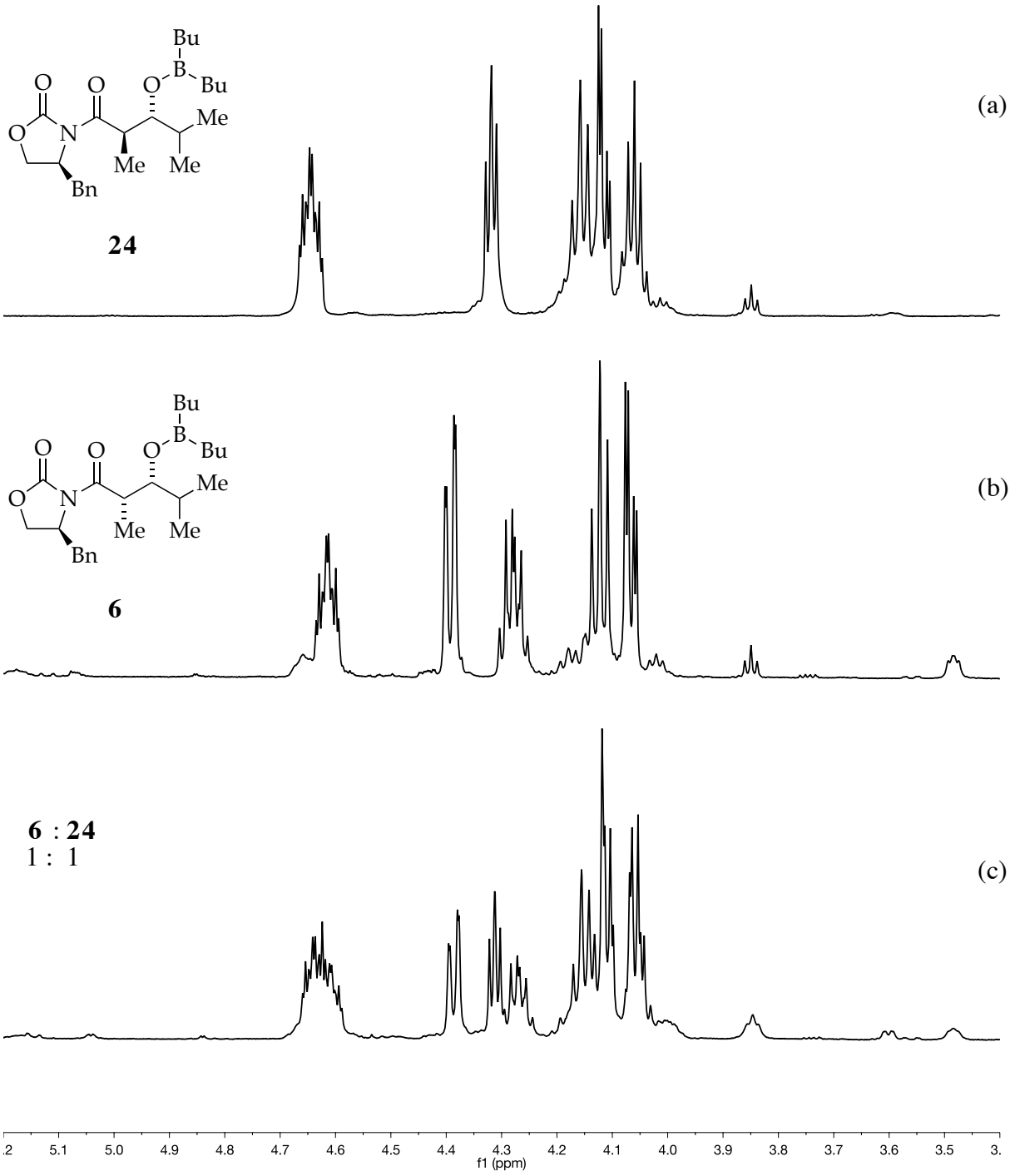
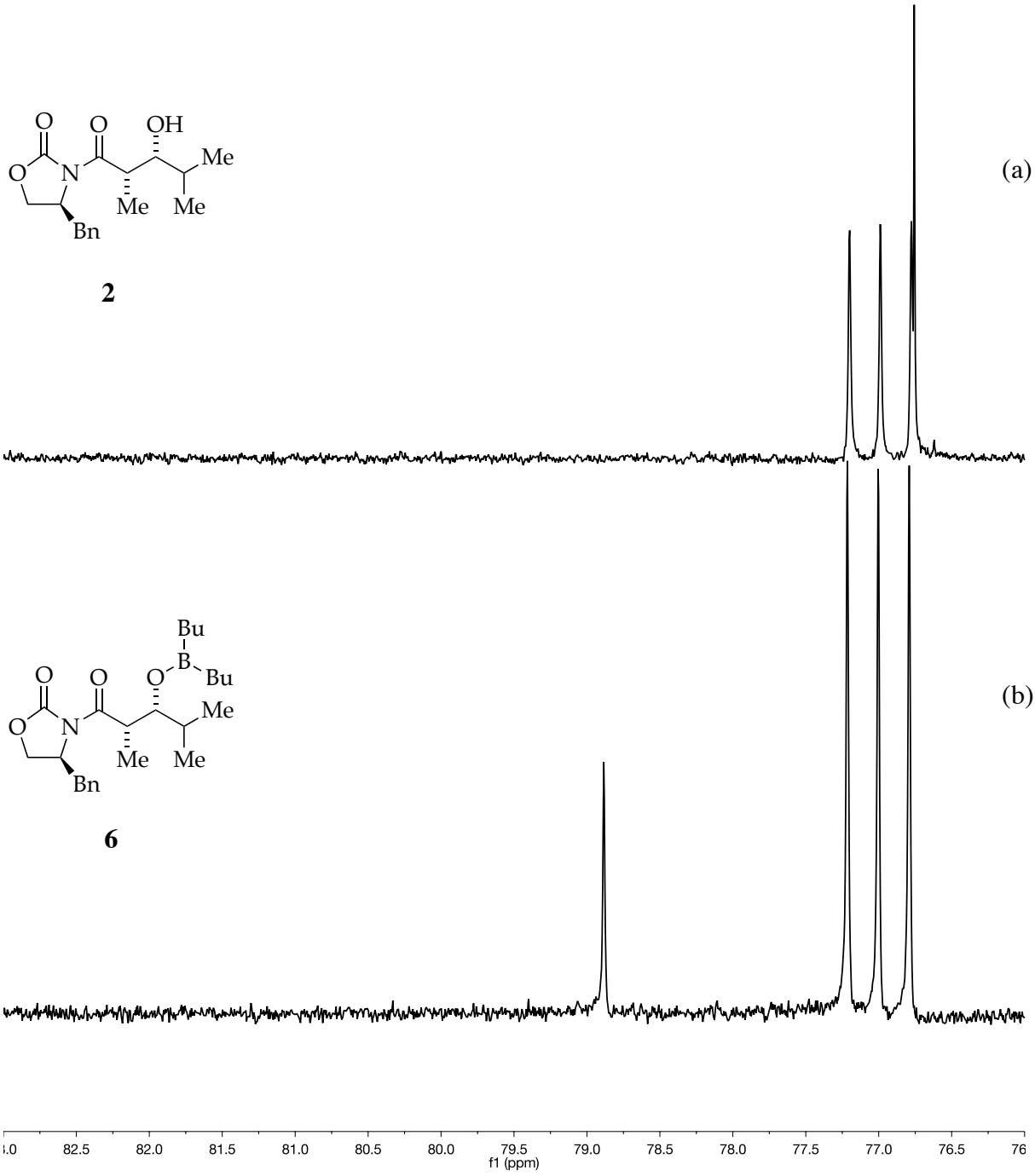


Figure A.1.21. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **2**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (b) 0.10 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (c) 0.050 M **2**, 0.050 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.



2

6

Figure A.1.22. ^{13}C NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **2**; (b) 0.10 M **2**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

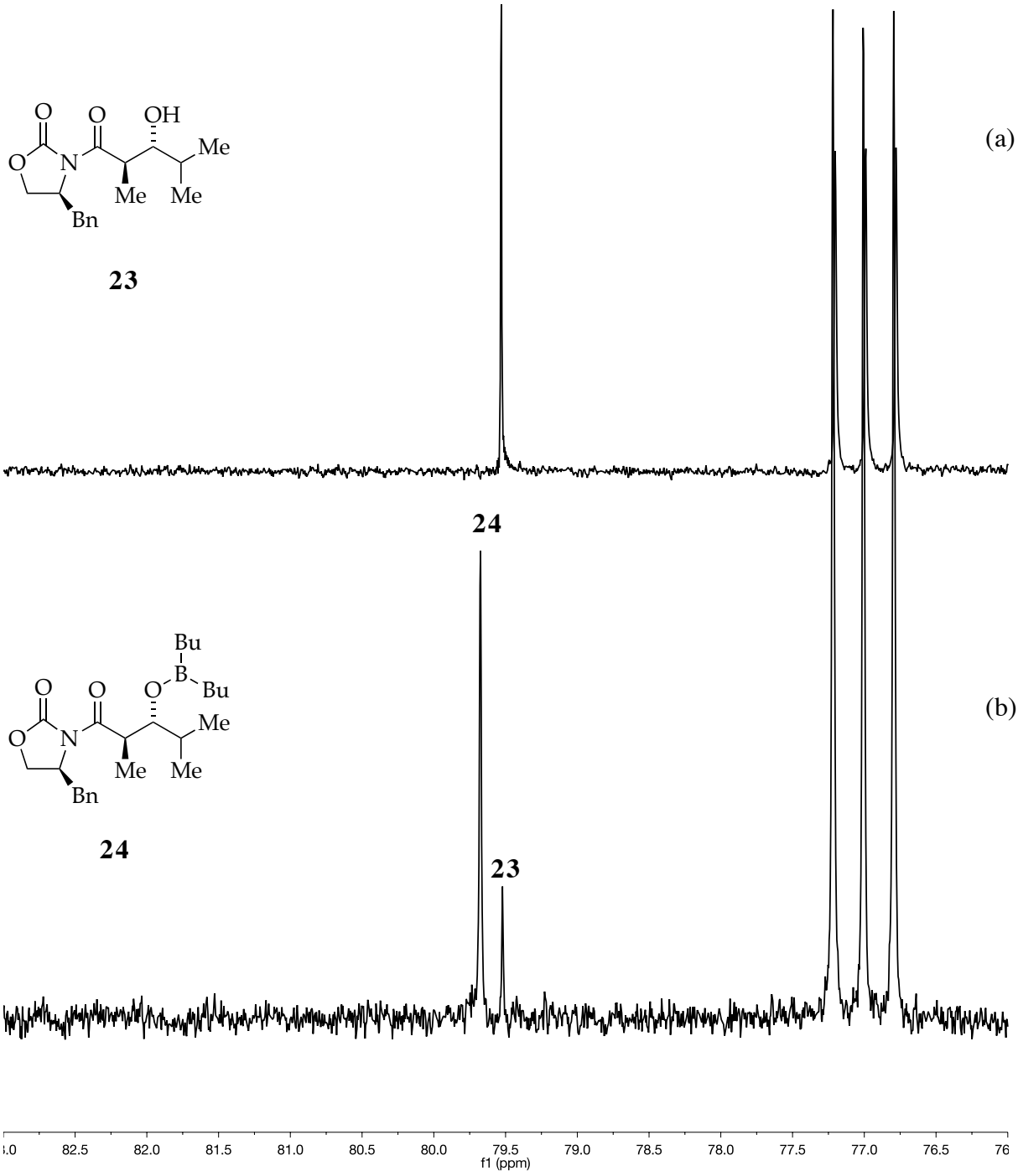


Figure A.1.23. ^{13}C NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **23**; (b) 0.10 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N.

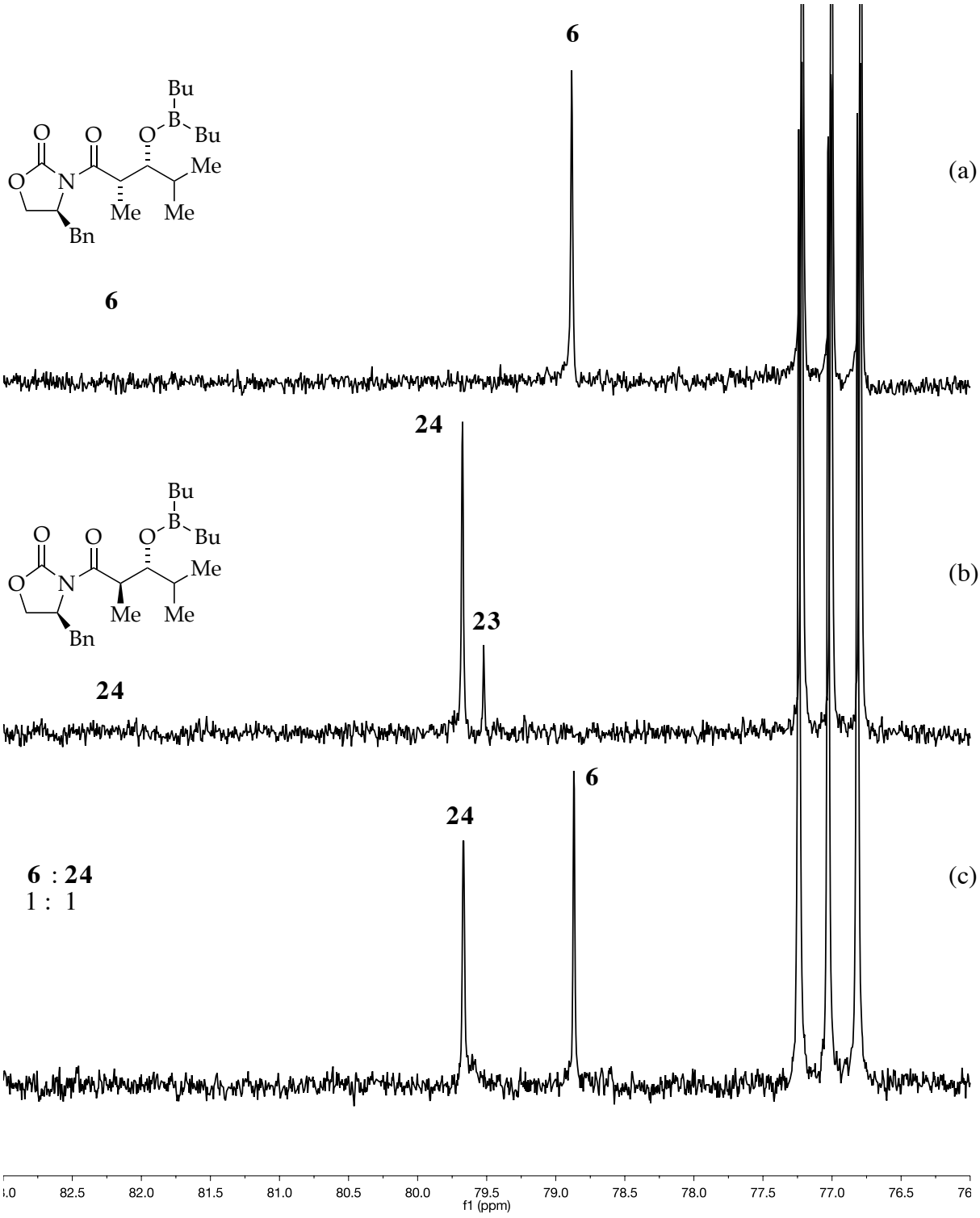


Figure A.1.24. ^{13}C NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **2**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (b) 0.10 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N; (c) 0.050 M **2**, 0.050 M **23**, 0.11 M Bu_2BOTf, and 0.12 M Et_3N in $CDCl_3$.

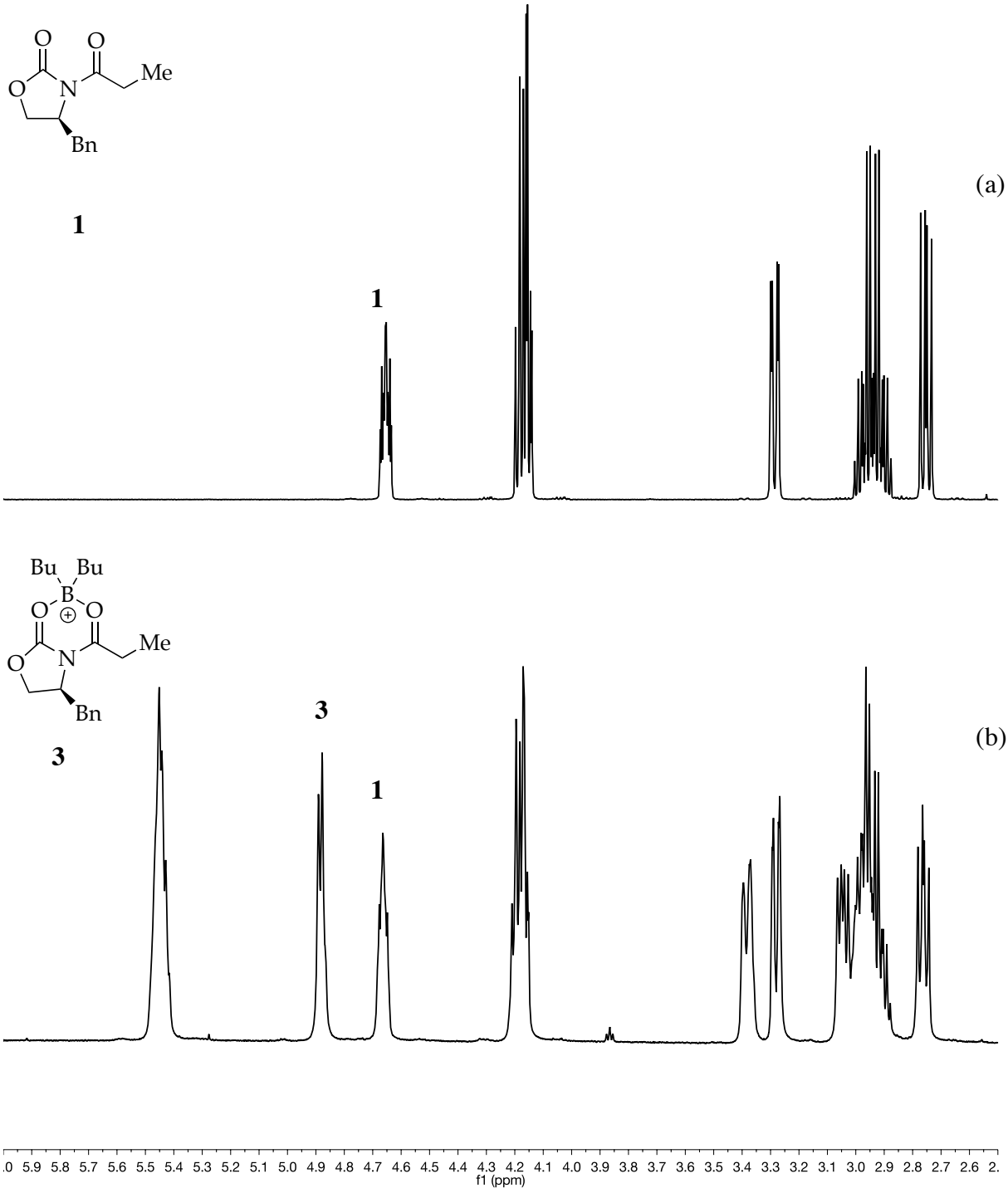


Figure A.1.25. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**; (b) 0.10 M **1** and 0.11 M Bu_2BOTf.

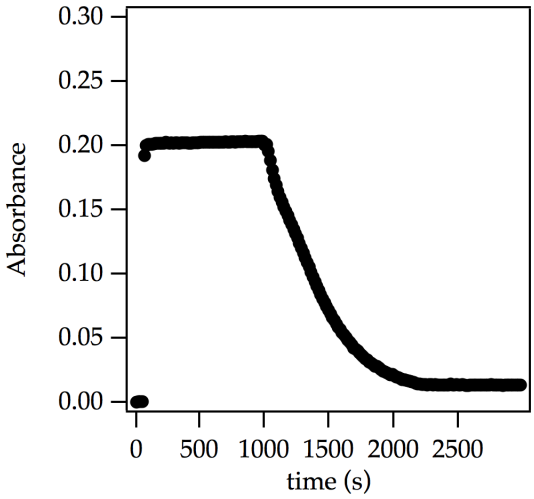


Figure A.1.26. IR spectra of injecting 3.3 equivalents of Bu_2BOTf over 33 minutes into 0.10 M **1** in $CHCl_3$, following loss of **1**. The curvature indicates soft equilibrium of complexation at room temperature.

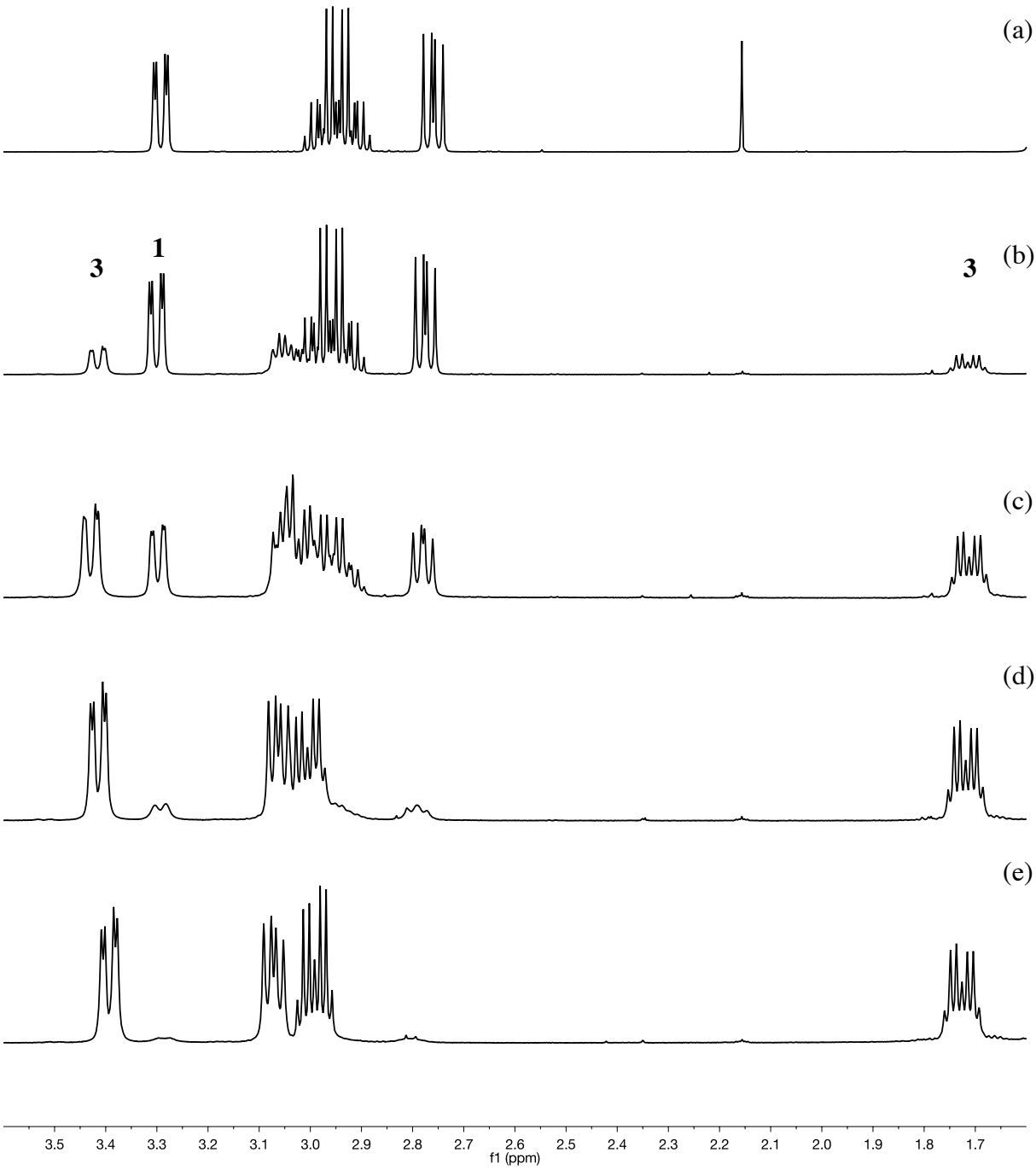


Figure A.1.27. ^{1}H NMR spectra in $CDCl_3$ recorded at rt: (a) 0.10 M **1**; (b) 0.10 M **1** and 0.05 M Bu_2BOTf; (c) 0.10 M **1** and 0.10 M Bu_2BOTf; (d) 0.10 M **1** and 0.20 M Bu_2BOTf; (e) 0.10 M **1** and 0.30 M Bu_2BOTf.

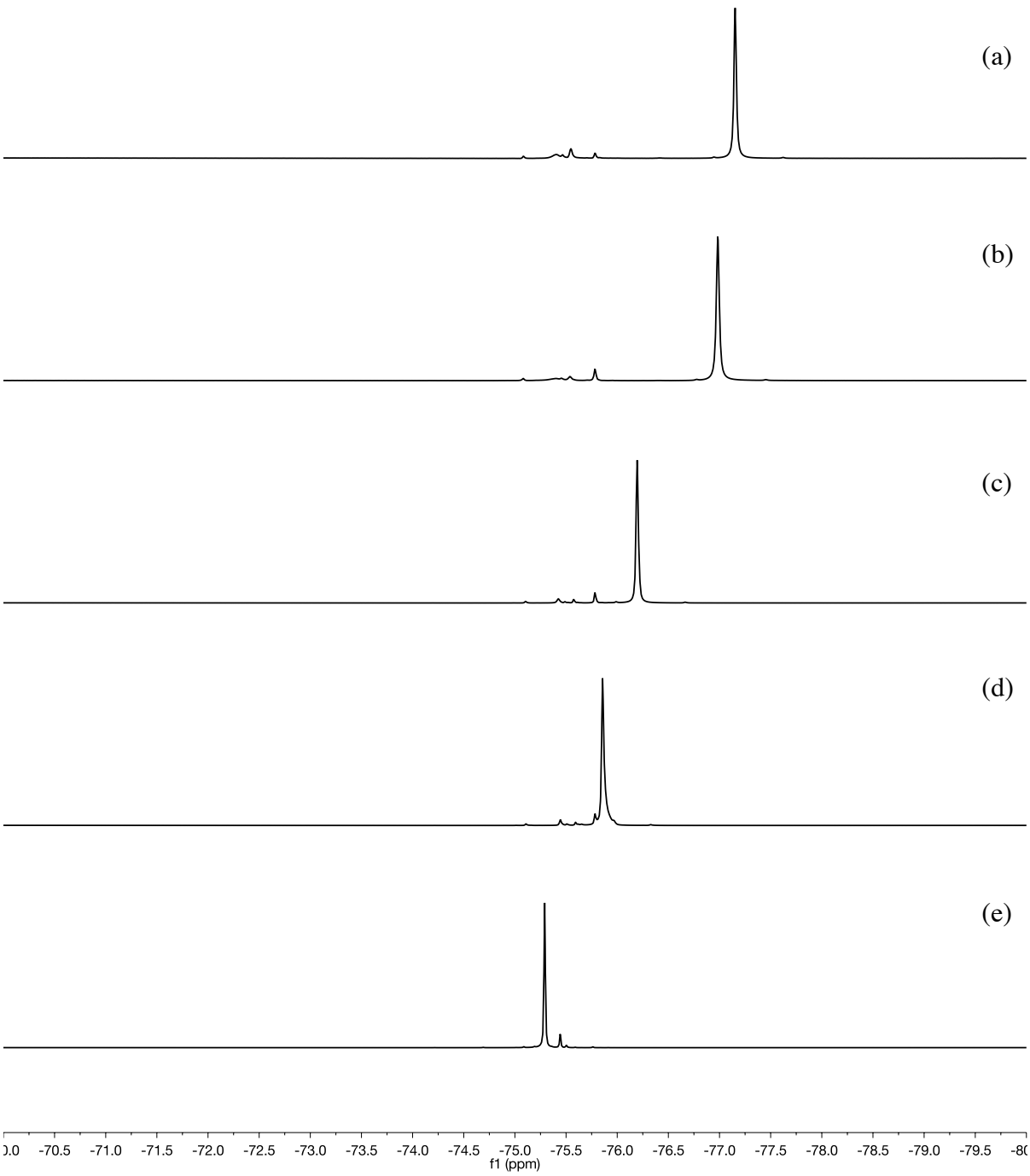


Figure A.1.28. ^{19}F NMR spectra in $CDCl_3$ recorded at –60 °C: (a) 0.10 M **1** and 0.05 M Bu_2BOTf; (b) 0.10 M **1** and 0.10 M Bu_2BOTf; (c) 0.10 M **1** and 0.20 M Bu_2BOTf; (d) 0.10 M **1** and 0.30 M Bu_2BOTf; (e) 0.10 M Bu_2BOTf.

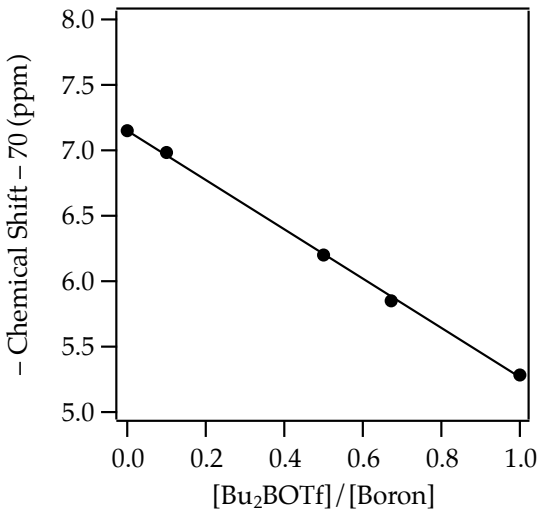


Figure A.1.29. Plot of ^{19}F NMR chemical shift vs. [Bu_2BOTf]/[Boron] for titrating **1** with Bu_2BOTf in $CDCl_3$ at –60 °C. $y = ax + b$, $a = -1.89 \pm 0.03$, $b = 7.15 \pm 0.02$.

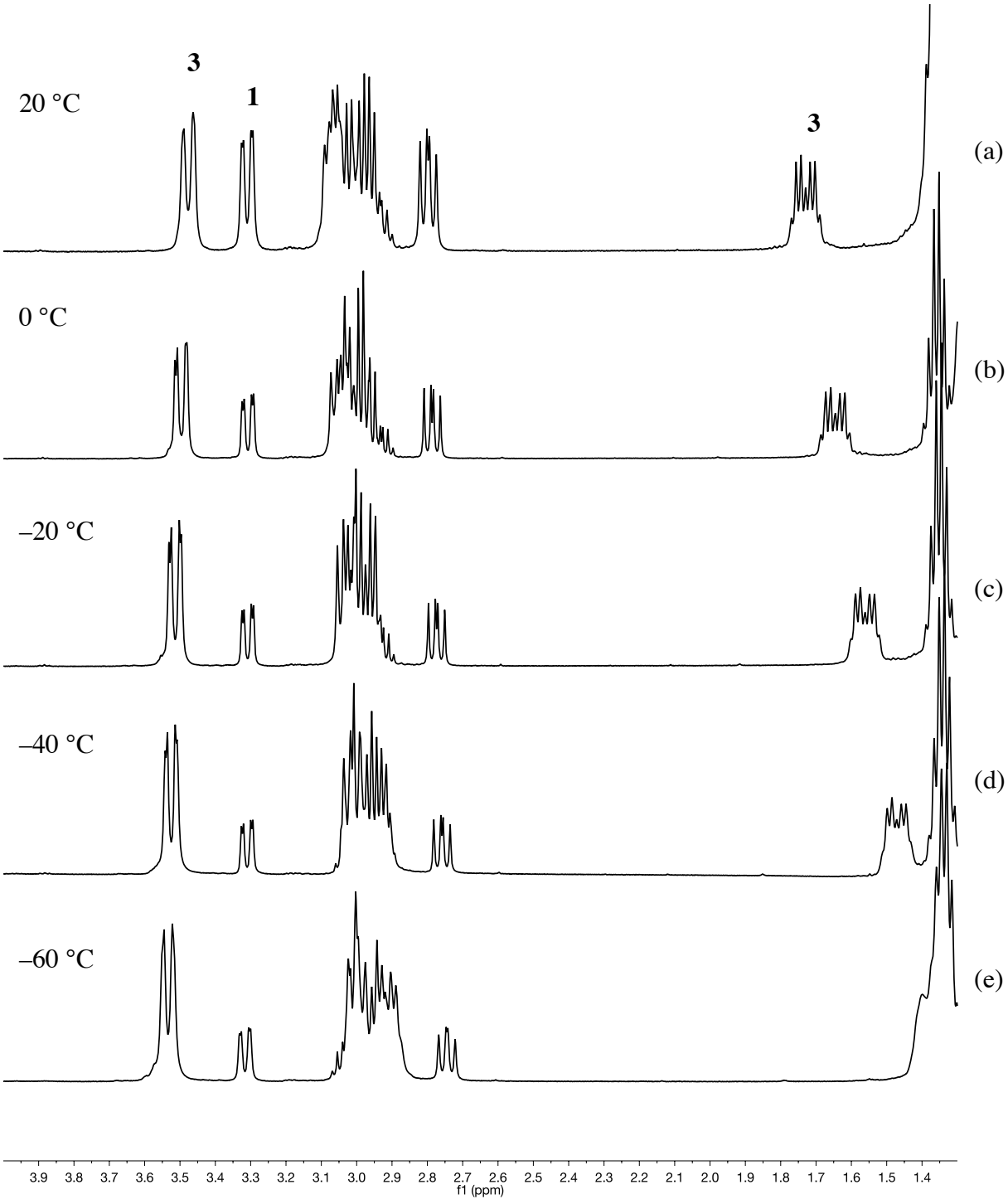


Figure A.1.30. ^{1}H NMR spectra of 0.20 M **1** and 0.15 M Bu_2BOTf in $CDCl_3$ recorded at: (a) 20 °C; (b) 0 °C; (c) –20 °C; (d) –40 °C; (e) –60 °C.

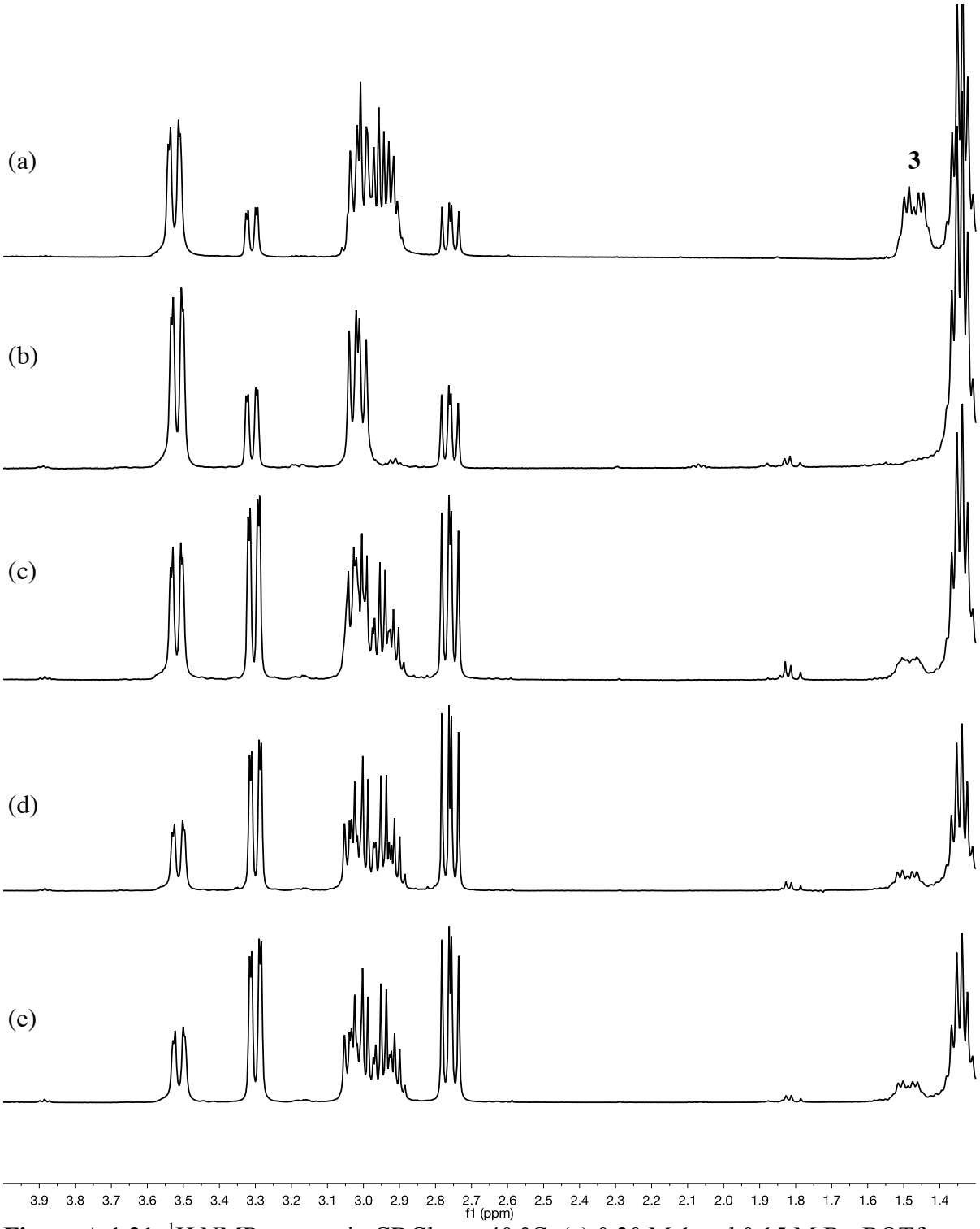


Figure A.1.31. ^{1}H NMR spectra in $CDCl_3$ at –40 °C: (a) 0.20 M **1** and 0.15 M Bu_2BOTf; (b) 0.20 M **1**-d_2 and 0.15 M Bu_2BOTf; (c) adding 0.20 M **1** into 0.20 M **1**-d_2 and 0.15 M Bu_2BOTf; (d) adding 0.20 M **1** into 0.20 M **1**-d_2 and 0.15 M Bu_2BOTf, votex at –40 °C; (e) adding 0.20 M **1** into 0.20 M **1**-d_2 and 0.15 M Bu_2BOTf, votex at –40 °C and age at rt for 10 minutes.

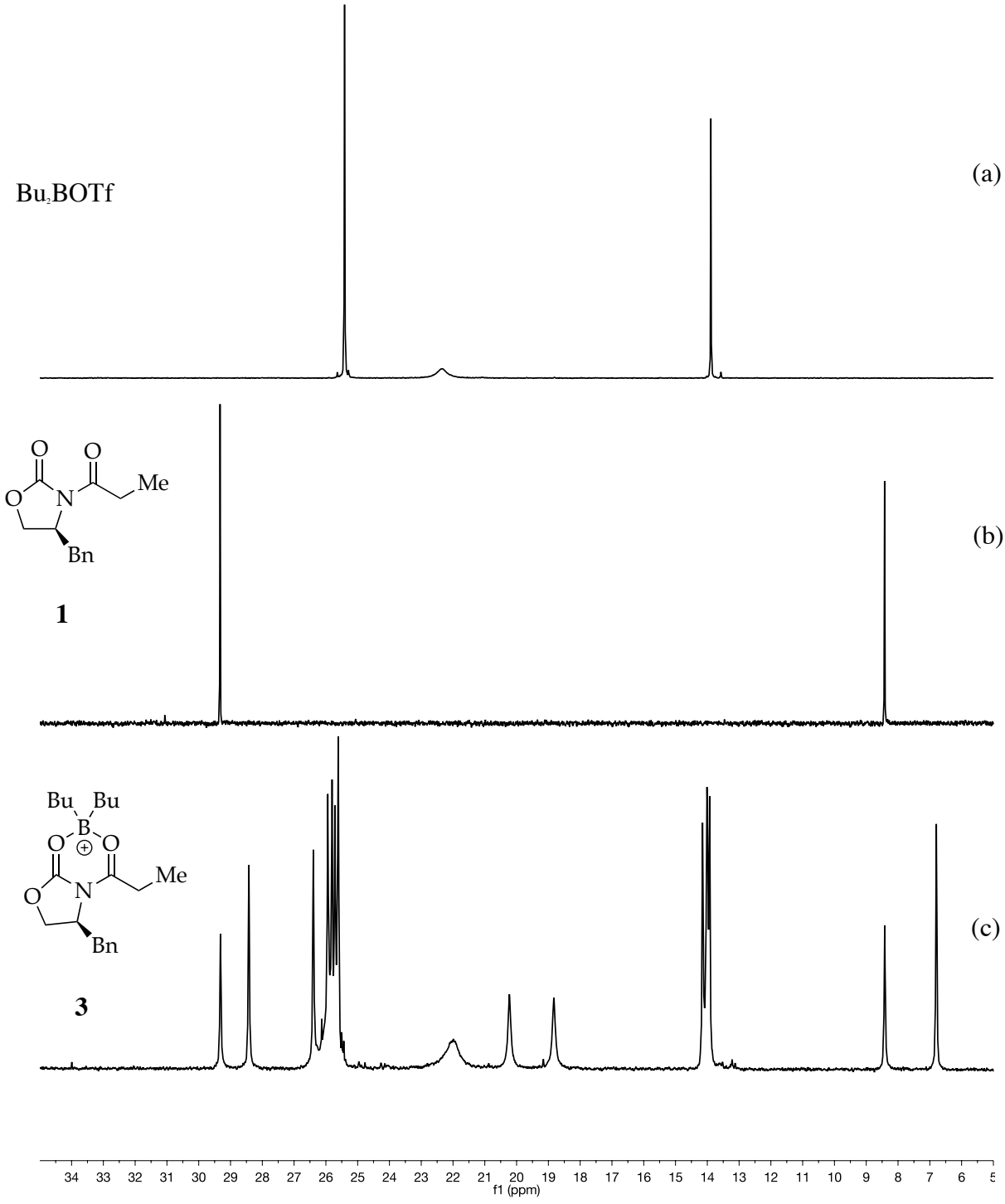


Figure A.1.32. ^{13}C NMR spectra in $CDCl_3$ at rt: (a) 0.20 M Bu_2BOTf; (b) 0.20 M **1**; (c) 0.20 M **1** and 0.20 M Bu_2BOTf.

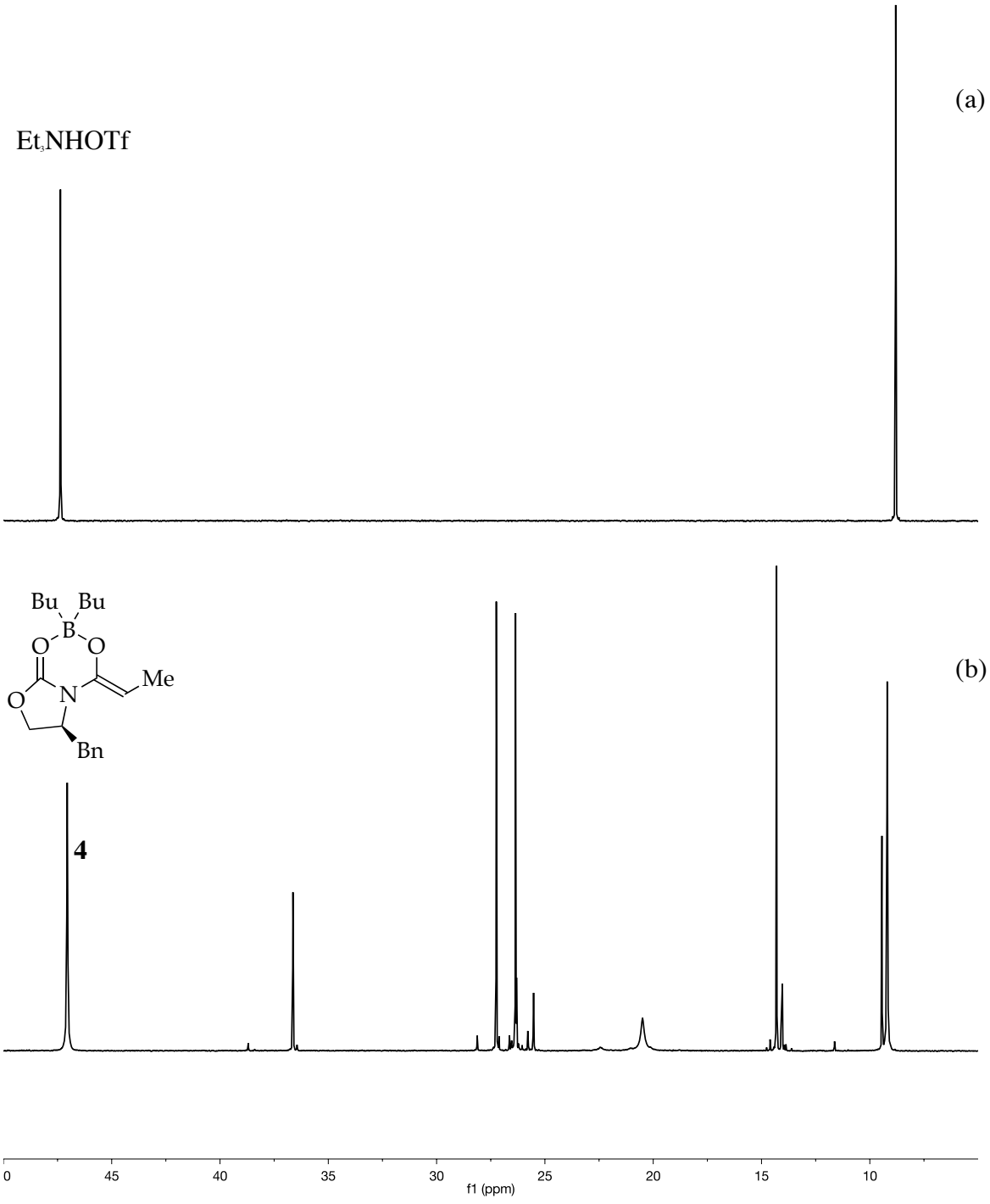


Figure A.1.33. ^{13}C NMR spectra in $CDCl_3$ at rt: (a) 0.20 M Et_3NHOTf; (b) 0.20 M **1**, 0.20 M Bu_2BOTf, and 0.20 M Et_3N.

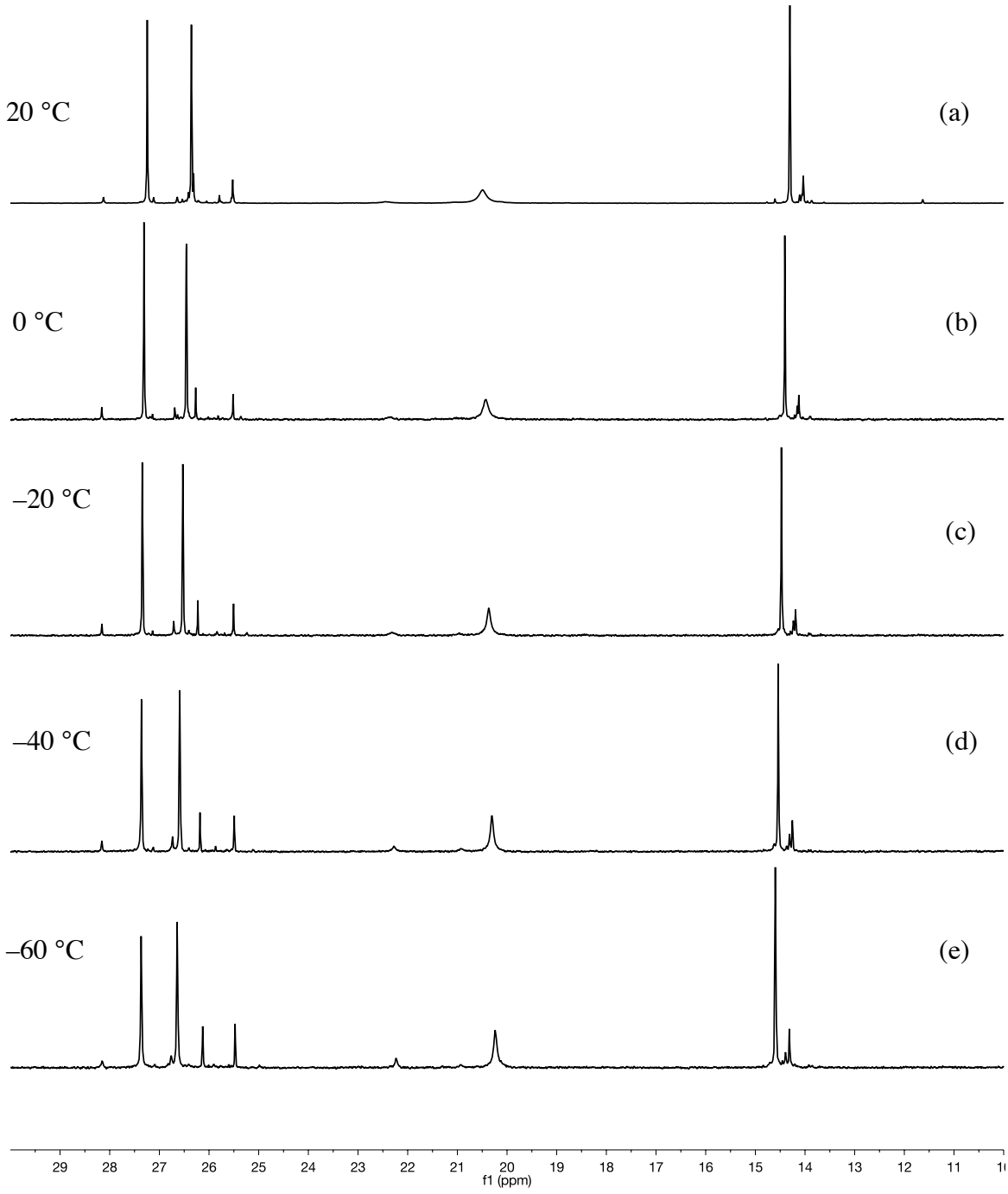


Figure A.1.34. ^{13}C NMR spectra of 0.20 M **1**, 0.20 M Bu_2BOTf and 0.20 M Et_2N in $CDCl_3$ recorded at: (a) 20 °C; (b) 0 °C; (c) –20 °C; (d) –40 °C; (e) –60 °C.

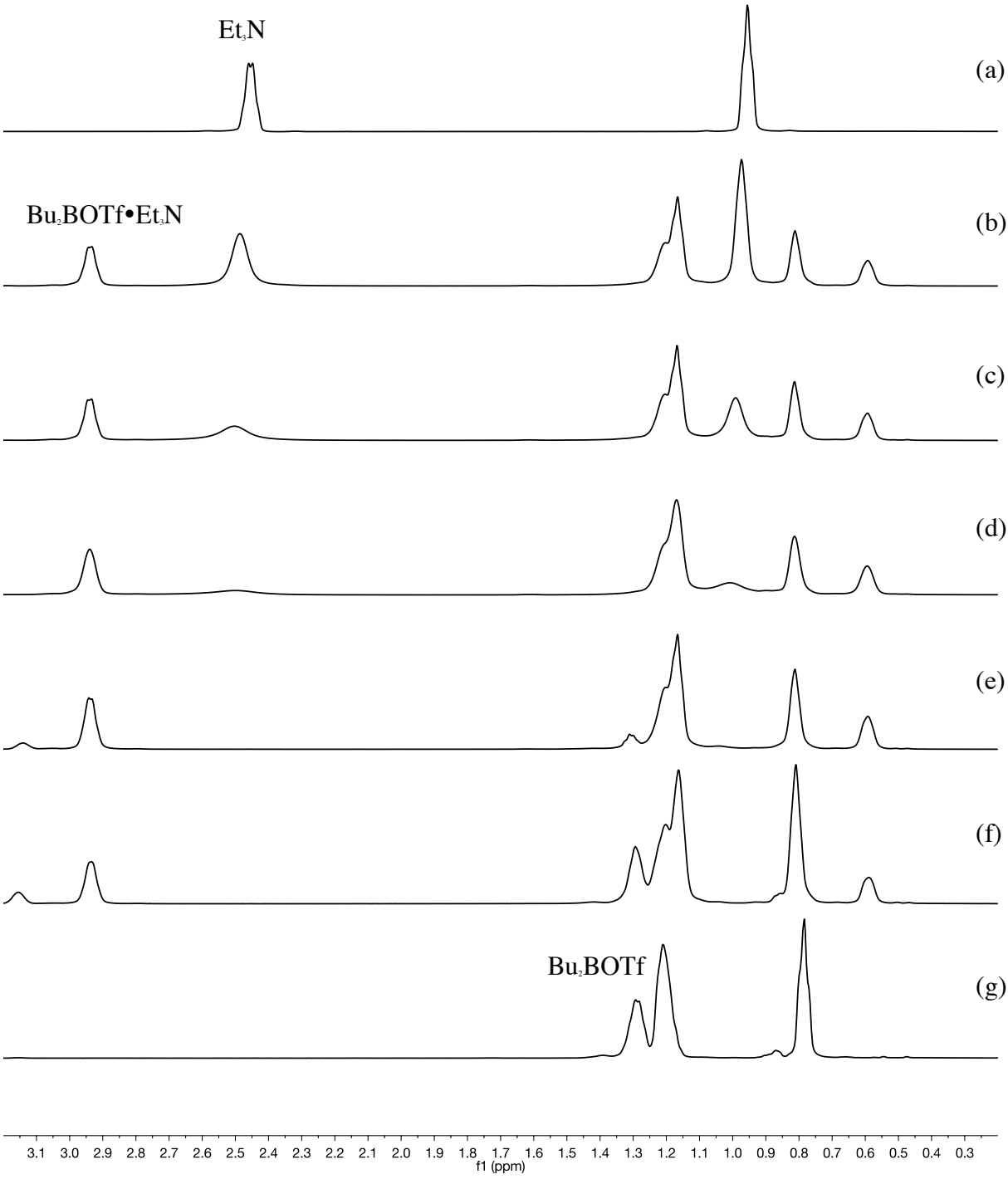


Figure A.1.35. ^{1}H NMR spectra in $CDCl_3$ recorded at –60 °C: (a) 0.10 M Et_3N; (b) 0.10 M Bu_2BOTf and 0.30 M Et_3N; (c) 0.10 M Bu_2BOTf and 0.20 M Et_3N; (d) 0.10 M Bu_2BOTf and 0.15 M Et_3N; (e) 0.10 M Bu_2BOTf and 0.10 M Et_3N; (f) 0.10 M Bu_2BOTf and 0.050 M Et_3N; (g) 0.10 M Bu_2BOTf.

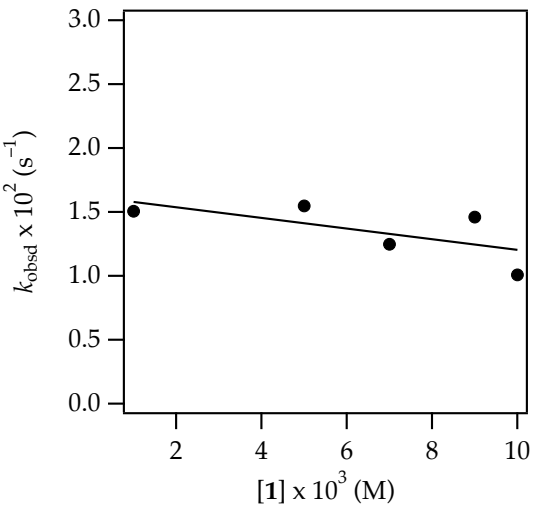


Figure A.1.36. Plot of observed rate vs [**1**] for enolization of [**1**] by Bu_2BOTf and Et_3N in $CHCl_3$ at 0 °C. $y = ax + b$, $a = -0.4 \pm 0.2$, $b = 0.016 \pm 0.002$.

[**1**] (M)	[$Bu_2BOTf \cdot Et_3N$] (M)	[Et_3N] (M)	k_{obsd} x 10^2 (s^{-1})
0.0010	0.10	0.20	1.51
0.0050	0.10	0.20	1.55
0.0070	0.10	0.20	1.25
0.0090	0.10	0.20	1.46
0.010	0.10	0.20	1.01

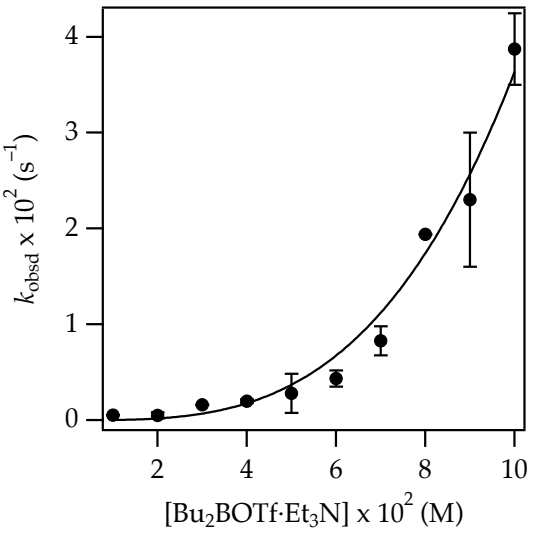


Figure A.1.37. Plot of observed rate vs [$Bu_2BOTf{\cdot}Et_3N$] for enolization of **1** by Bu_2BOTf and Et_3N in $CHCl_3$ at 0 °C. $y = ax^b + c$, $a = 72 \pm 3$, $b = 3.3 \pm 0.3$, c set to 0.0

[**1**] (M)	[$Bu_2BOTf{\cdot}Et_3N$] (M)	[Et_3N] (M)	k_{obsd} x 10^3 (s^{-1})
0.0020	0.010	0.10	0.538
0.0020	0.020	0.10	0.498
0.0020	0.030	0.10	1.59
0.0020	0.040	0.10	1.97
0.0020	0.050	0.10	2.79
0.0020	0.060	0.10	4.34
0.0020	0.070	0.10	8.28
0.0020	0.080	0.10	19.4
0.0020	0.090	0.10	23.0
0.0020	0.10	0.10	38.7

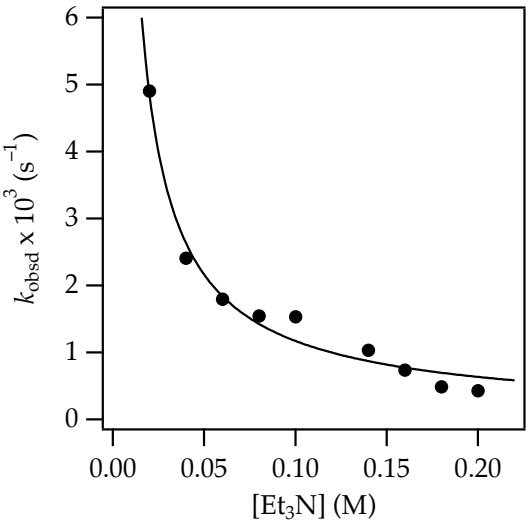


Figure A.1.38. Plot of observed rate vs added [Et_3N] for enolization of **1** by Bu_2BOTf and Et_3N in $CHCl_3$ at 0 °C. $y = ax^b + c$, $a = 0.00015 \pm 0.00003$, b = –0.88 ± 0.05, c set to 0.00

[**1**] (M)	[$Bu_2BOTf{\cdot}Et_3N$] (M)	[Et_3N] (M)	k_{obsd} x 10^3 (s^{-1})
0.0020	0.040	0.020	4.91
0.0020	0.040	0.040	2.41
0.0020	0.040	0.060	1.79
0.0020	0.040	0.080	1.55
0.0020	0.040	0.10	1.53
0.0020	0.040	0.14	1.03
0.0020	0.040	0.16	0.737
0.0020	0.040	0.18	0.487
0.0020	0.040	0.20	0.429

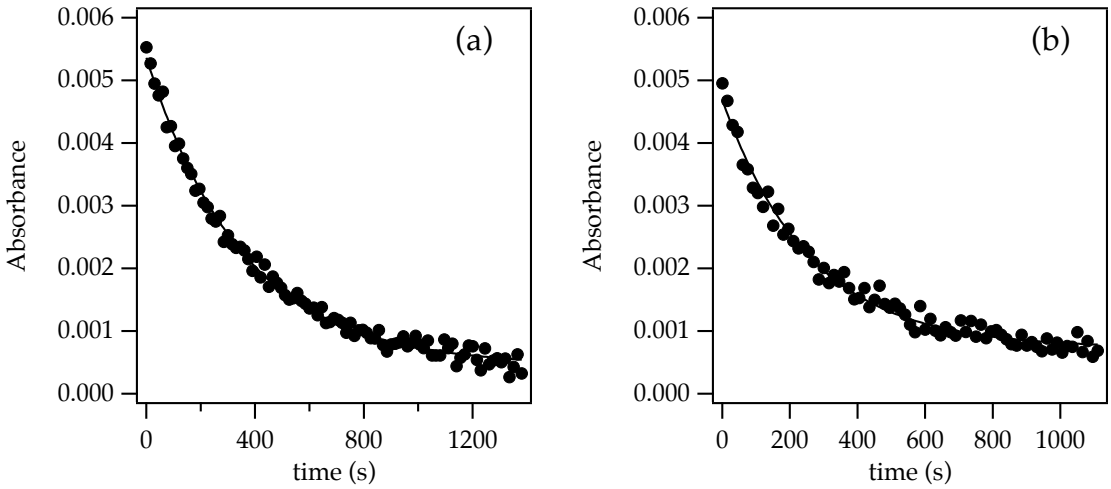


Figure A.1.39. IR spectra in $CHCl_3$ at 0 °C, following loss of **1**: (a) injecting 0.0030 M **1** into pre-mixed 0.050 M Bu_2BOTf and 0.10 M Et_3N, k_{obsd} = 0.003 s^{-1}; (b) injecting 0.0030 M **1**-$\boldsymbol{d}_2$ into pre-mixed 0.050 M Bu_2BOTf and 0.10 M Et_3N, k_{obsd} = 0.003 s^{-1}.

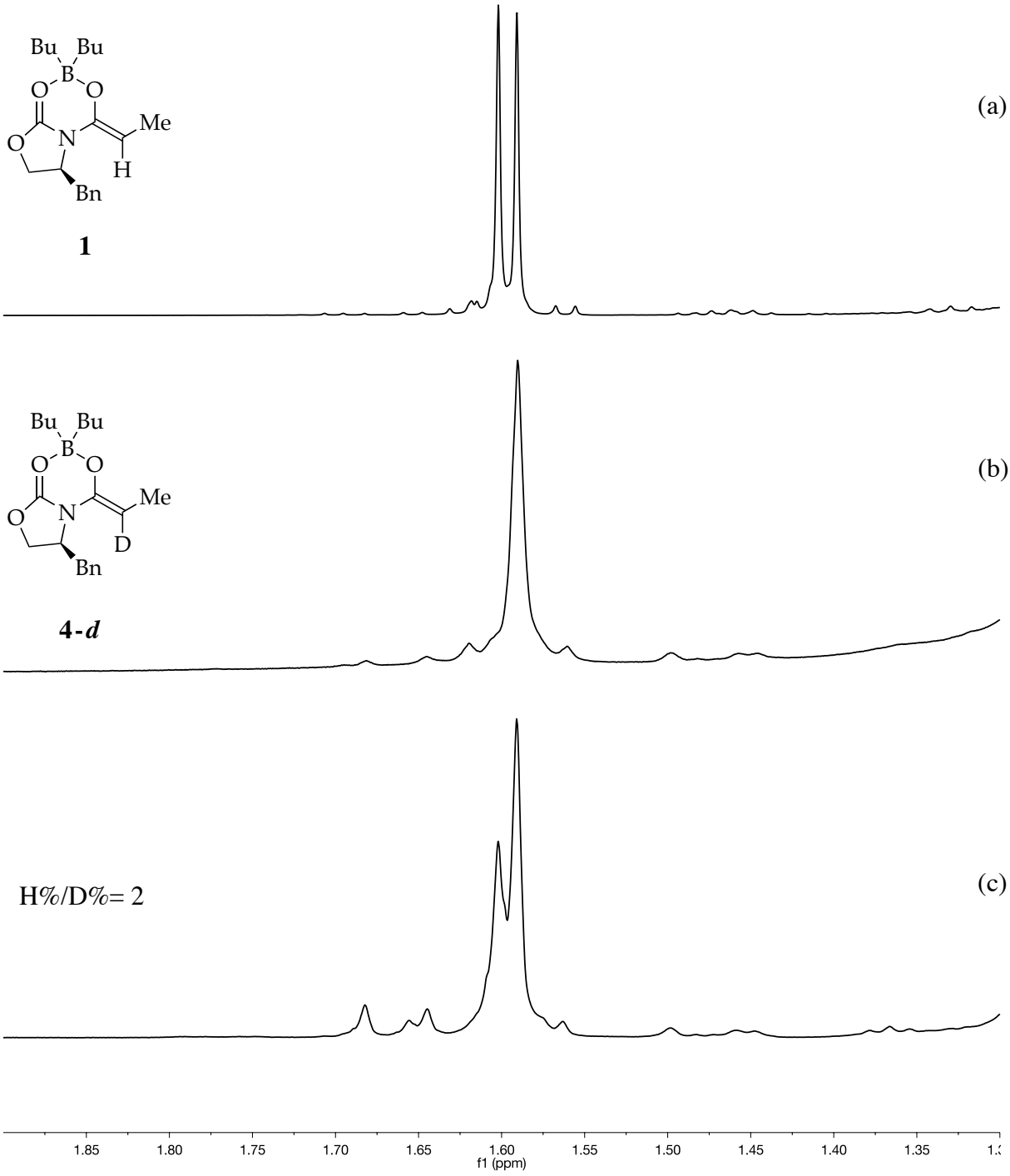


Figure A.1.40. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.040 M Bu_2BOTf, and 0.040 M Et_3N; (b) 0.10 M **1**-d_2, 0.040 M Bu_2BOTf, and 0.040 M Et_3N; (c) injecting pre-mixed 0.10 M **1** and 0.10 M **1**-d_2 into pre-mixed 0.040 M Bu_2BOTf and 0.040 M Et_3N. $k_H/k_D = 2$

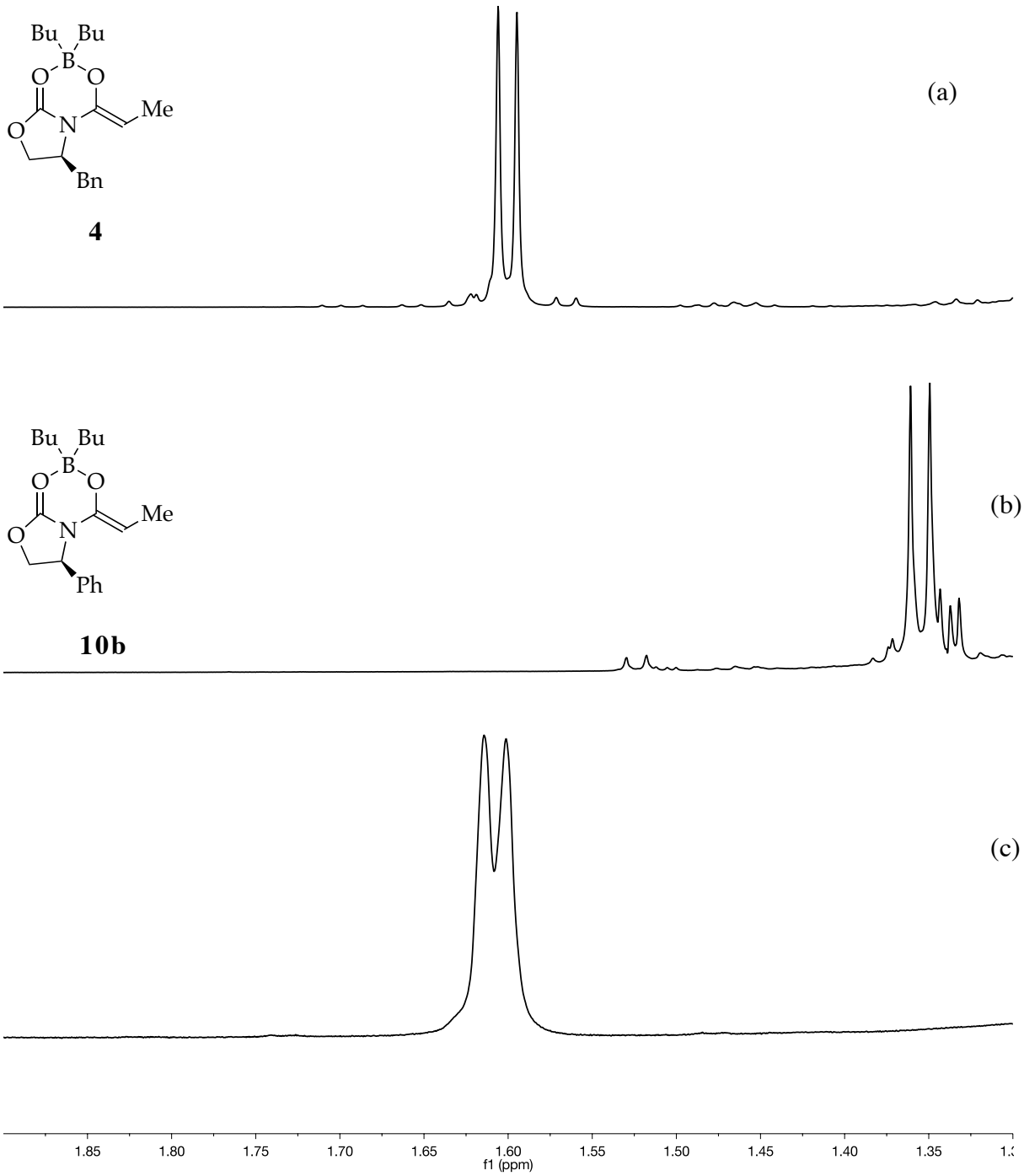


Figure A.1.41. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (b) 0.10 M **10**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (c) injecting 0.10 M **10** into pre-mixed 0.10 M **1**, 0.050 M Bu_2BOTf, and 0.10 M Et_3N.

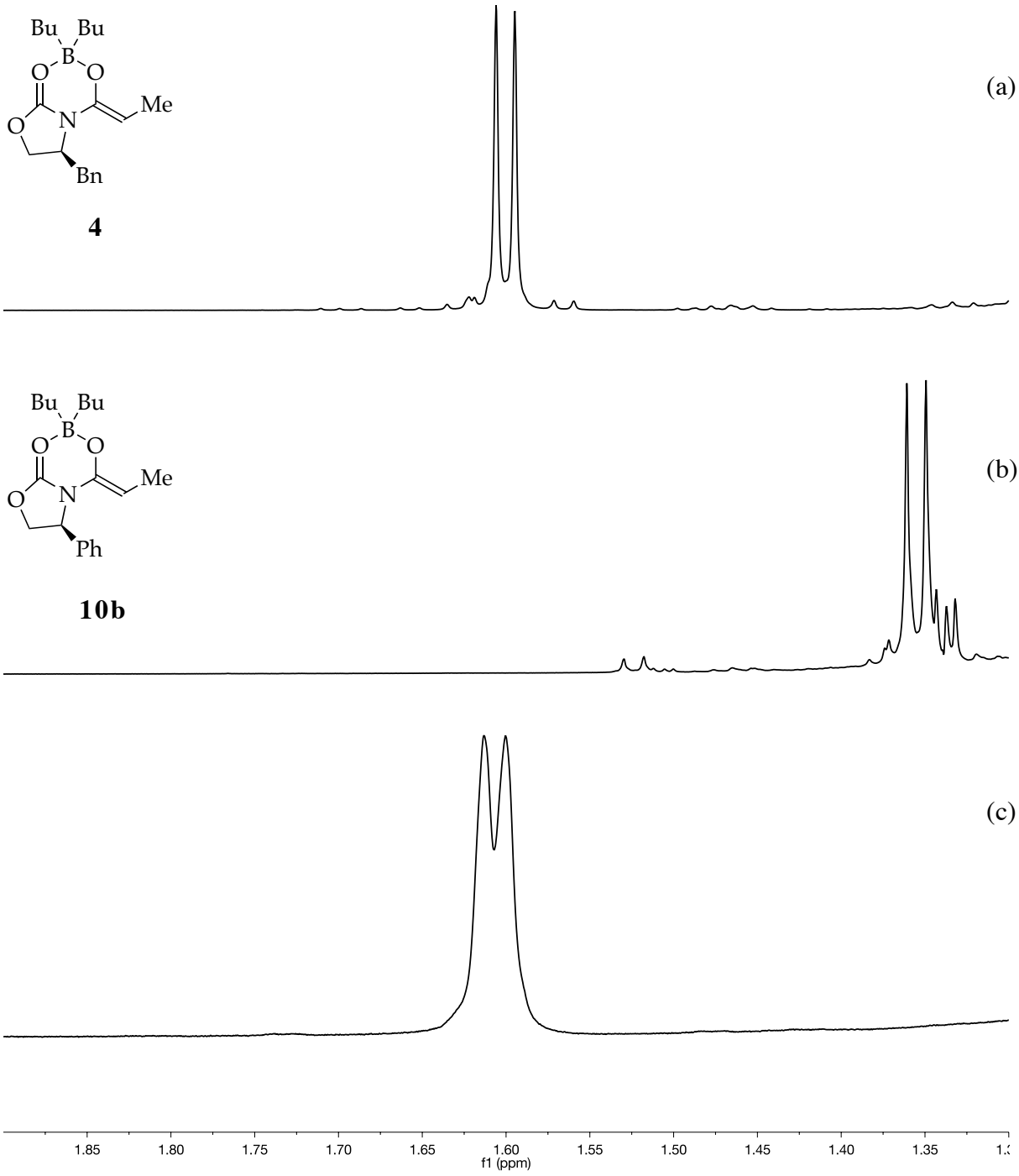


Figure A.1.42. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (b) 0.10 M **10**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (c) injecting pre-mixed 0.10 M **1** and 0.050 M Bu_2BOTf into pre-mixed 0.10 M Et_3N and 0.10 M **10**.

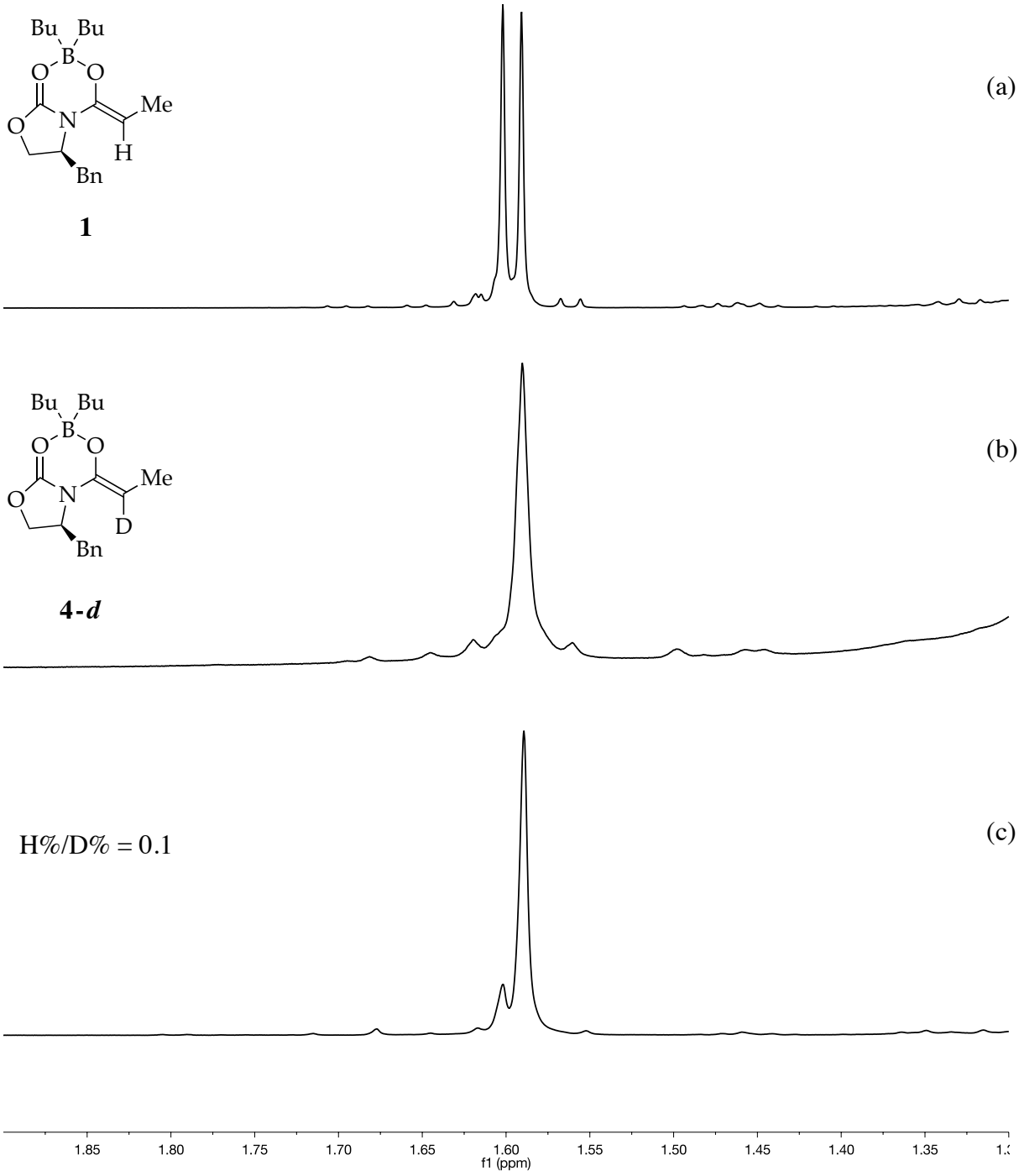


Figure A.1.43. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (b) 0.10 M **1**-d_2, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (c) injecting pre-mixed 0.10 M **1**-d_2 and 0.050 M Bu_2BOTf into pre-mixed 0.10 M Et_3N and 0.10 M **1**. H%/D% = 0.1.

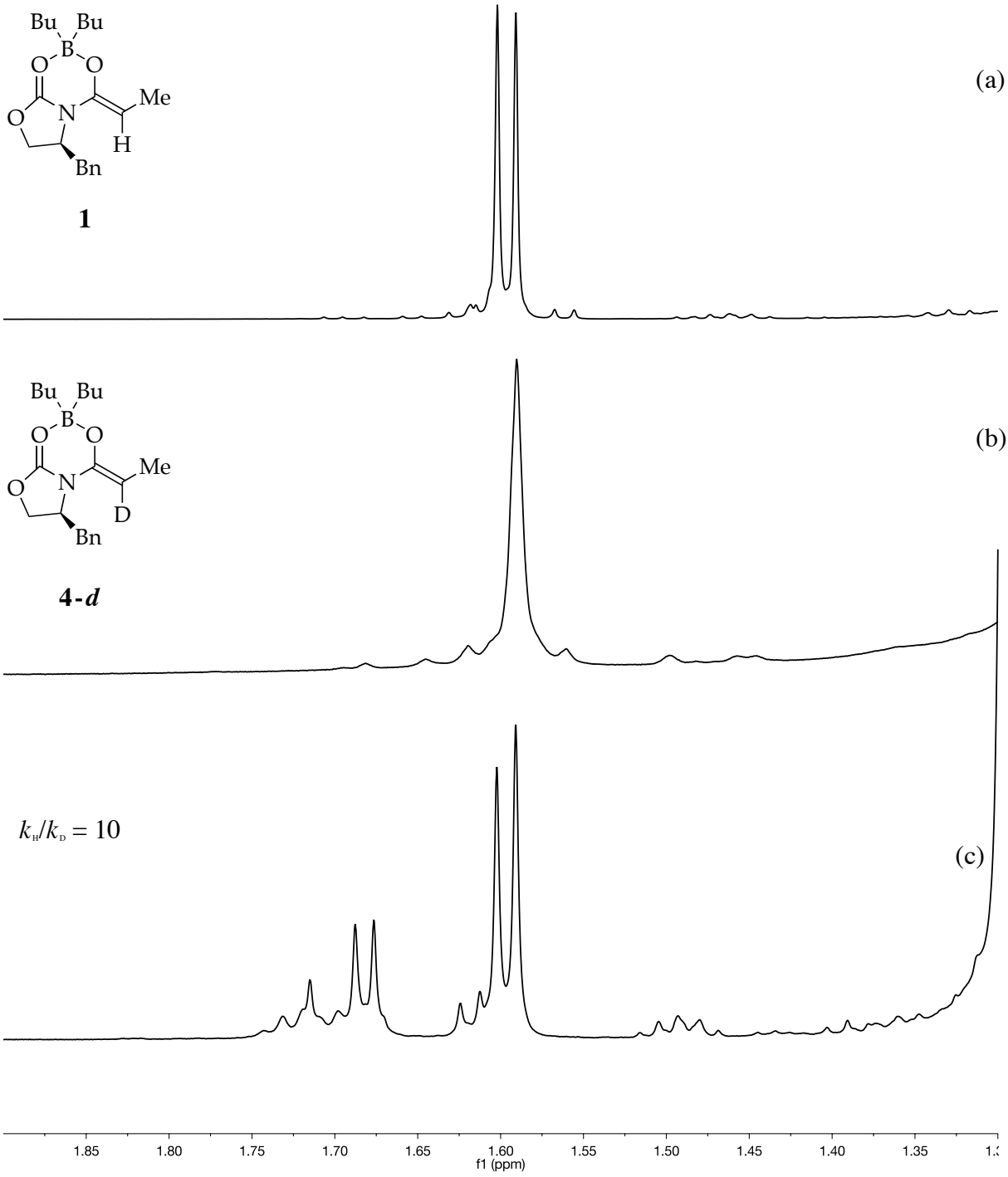


Figure A.1.44. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (b) 0.10 M **1**-d_2, 0.10 M Bu_2BOTf, and 0.10 M Et_3N; (c) injecting 0.080 M Et_3N into pre-mixed 0.10 M **1**-d_2, 0.10 M **1**, and 0.20 M Bu_2BOTf. k_H/k_D= 10.

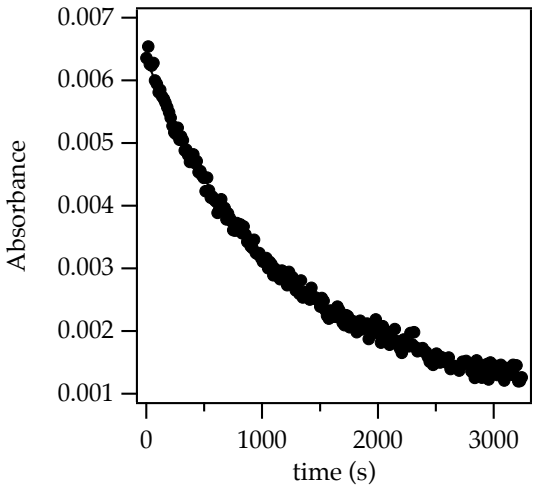


Figure A.1.45. IR spectra of injecting 0.0040 M **1** into pre-mixed 0.050 M Bu_2BOTf and 0.15 M Et_3N in $CHCl_3$ recorded at 0 °C, following loss of **1**. $k_{obsd} = 9.9 \times 10^{-4}$ s^{-1}.

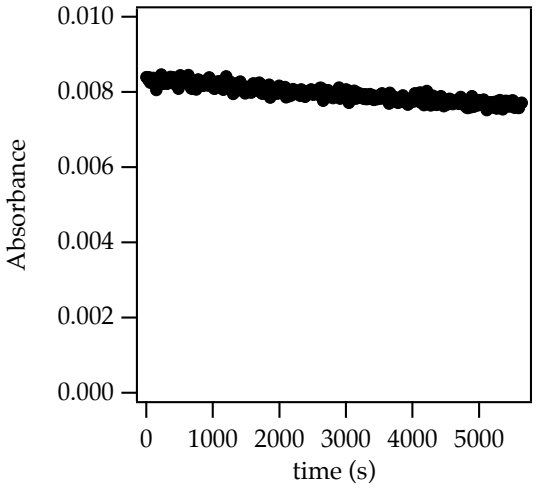


Figure A.1.46. IR spectra of injecting 0.0050 M **1** into pre-mixed 0.050 M Bu_2BOTf and 0.15 M Et_2NMe in $CHCl_3$ recorded at 0 °C, following loss of **1**. $k_{obsd} = 3.1 \times 10^{-5}$ s^{-1}, $k_{rel} = 0.03$.

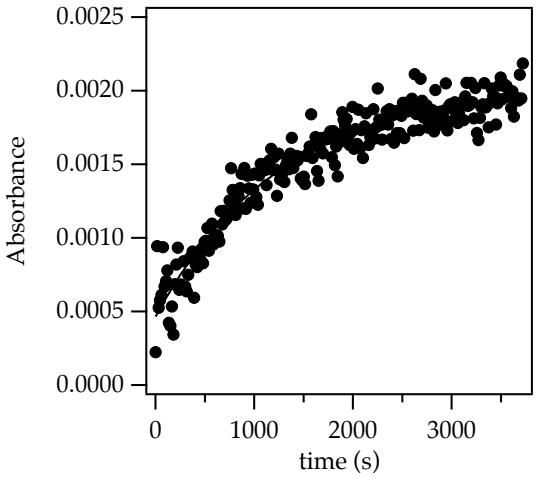


Figure A.1.47. IR spectra of injecting 0.0040 M **1** into pre-mixed 0.050 M Bu_2BOTf and 0.15 M Me_2NCy in $CHCl_3$ recorded at 0 °C, following growth of **4**. k_{obsd}= 8.0 x 10^{-5} s^{-1}, k_{rel} = 0.8.

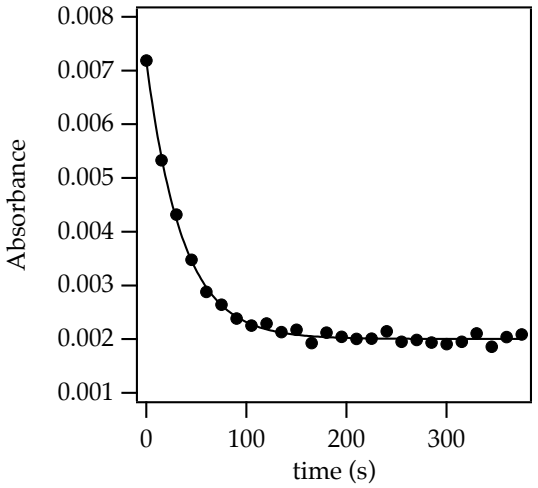


Figure A.1.48. IR spectra of injecting 0.0040 M **1** into pre-mixed 0.050 M Bu_2BOTf and 0.15 M *i*-Pr_2NEt in $CHCl_3$ recorded at 0 °C, following loss of **1**. k_{obsd} = 2.8 x 10^{-2} s^{-1}, k_{rel} = 30.

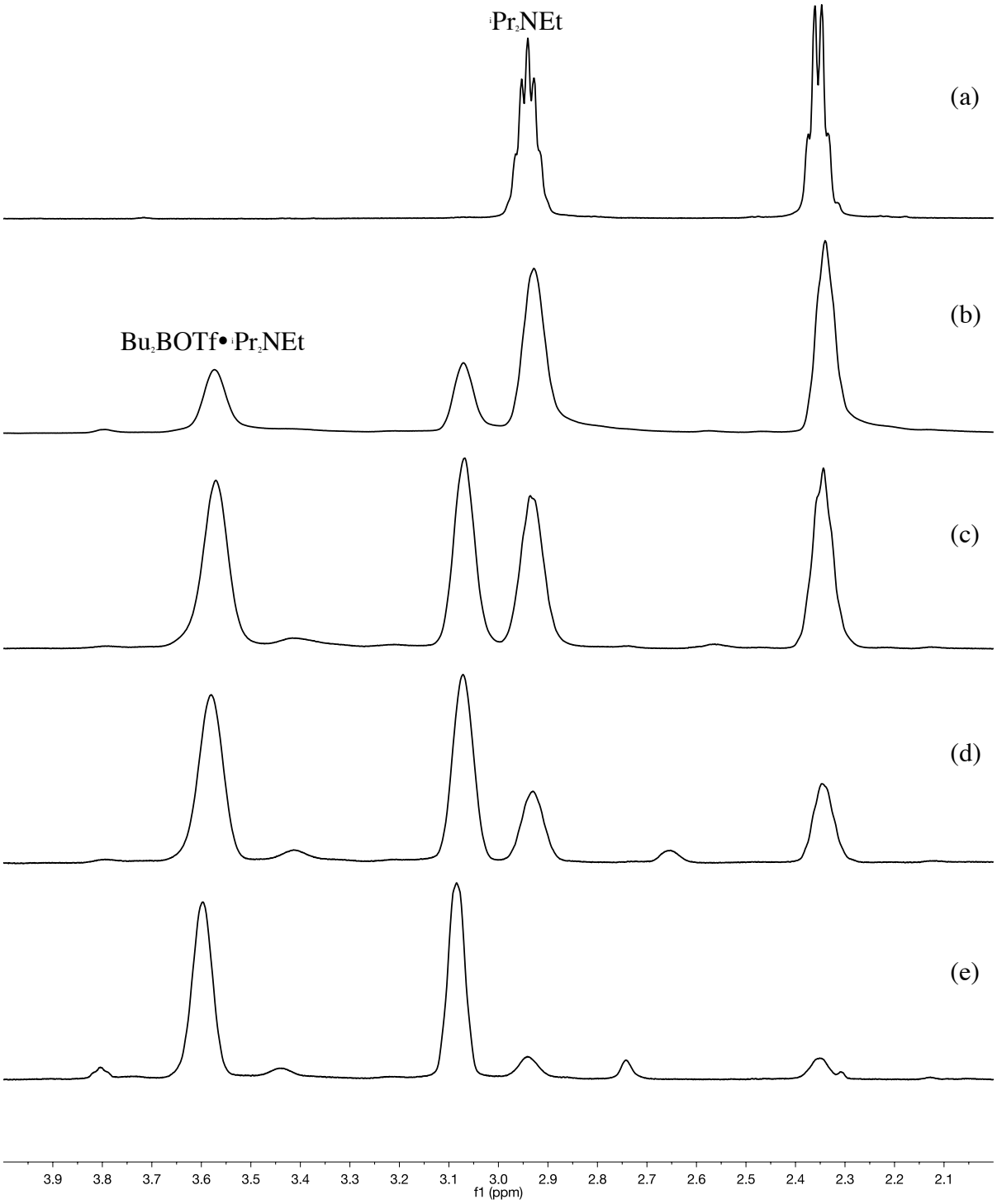


Figure A.1.49. ^{1}H NMR spectra in $CDCl_3$ recorded at –60 °C: (a) 0.10 M $^{i}Pr_2NEt$; (b) 0.10 M Bu_2BOTf and 0.30 M $^{i}Pr_2NEt$; (c) 0.10 M Bu_2BOTf and 0.20 M $^{i}Pr_2NEt$; (d) 0.10 M Bu_2BOTf and 0.15 M $^{i}Pr_2NEt$; (e) 0.10 M Bu_2BOTf and 0.10 M $^{i}Pr_2NEt$.

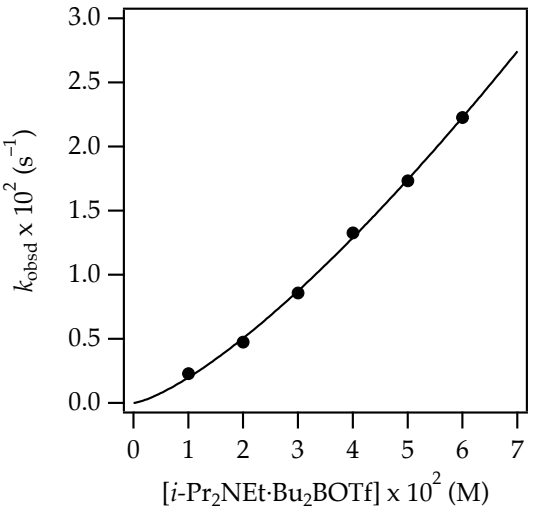


Figure A.1.50. Plot of observed rate vs added [i-$Pr_2NEt{\cdot}Bu_2BOTf$] for enolization of **1** by Bu_2BOTf and i-Pr_2NEt in $CHCl_3$ at 0 °C. $y = ax^b + c$, $a = 0.99 \pm 0.10$, $b = 1.35 \pm 0.03$, c set to 0.00.

[**1**] (M)	[i-$Pr_2NEt{\cdot}Bu_2BOTf$] (M)	[i-Pr_2NEt] (M)	k_{obsd} x 10^2 (s^{-1})
0.002	0.010	0.20	0.229
0.002	0.020	0.20	0.475
0.002	0.030	0.20	0.859
0.002	0.040	0.20	1.33
0.002	0.050	0.20	1.73
0.002	0.060	0.20	2.23

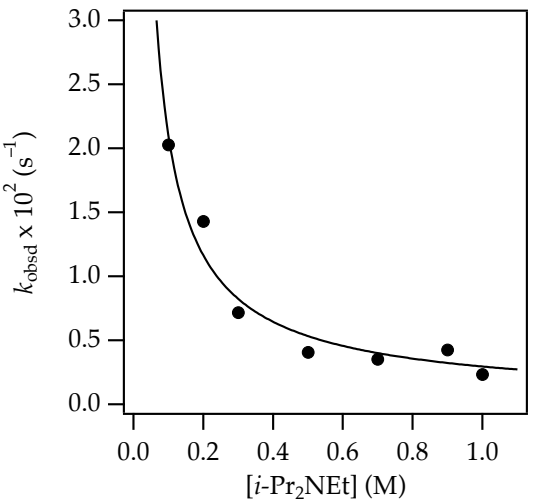


Figure A.1.51. Plot of observed rate vs added [*i*-Pr_2NEt] for enolization of **1** by Bu_2BOTf and *i*-Pr_2NEt in $CHCl_3$ at 0 °C. $y = ax^b + c$, $a = 0.0030 \pm 0.0006$, $b = -0.85 \pm 0.09$, c set to 0.00.

[**1**] (M)	[*i*-Pr_2NEt·Bu_2BOTf] (M)	[*i*-Pr_2NEt] (M)	k_{obsd} x10^2 (s^{-1})
0.0020	0.040	0.10	2.03
0.0020	0.040	0.20	1.43
0.0020	0.040	0.30	0.716
0.0020	0.040	0.50	0.407
0.0020	0.040	0.70	0.353
0.0020	0.040	0.90	0.426
0.0020	0.040	1.00	0.233

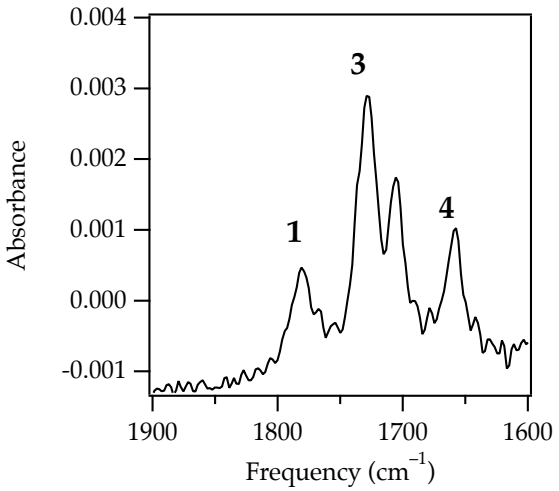


Figure A.1.52. IR spectra of 0.0020 M **1**, 0.050 M Bu_2BOTf, and 0.15 M *i*-Bu_3N in $CHCl_3$ recorded at 0 °C.

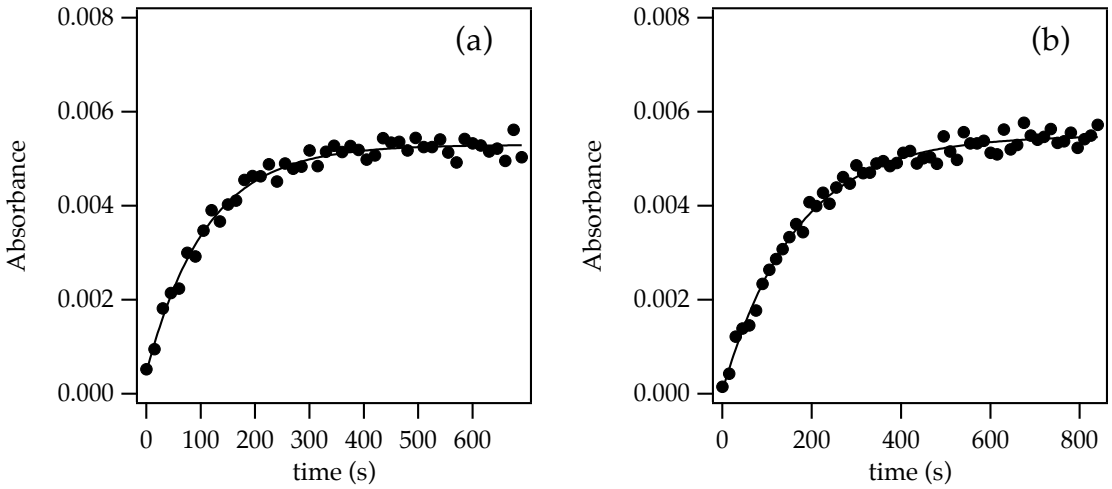


Figure A.1.53. IR spectra in $CHCl_3$ recorded at 0 °C: (a) injecting 0.060 M *i*-Bu_3N into pre-mixed 0.040 M Bu_2BOTf and 0.0020 M **1**, following growth of **4**, k_{obsd} = 0.009 s^{-1}; (b) injecting 0.0020 M **1** into pre-mixed 0.040 M Bu_2BOTf and 0.060 M *i*-Bu_3N, following growth of **4**, k_{obsd} = 0.009 s^{-1}.

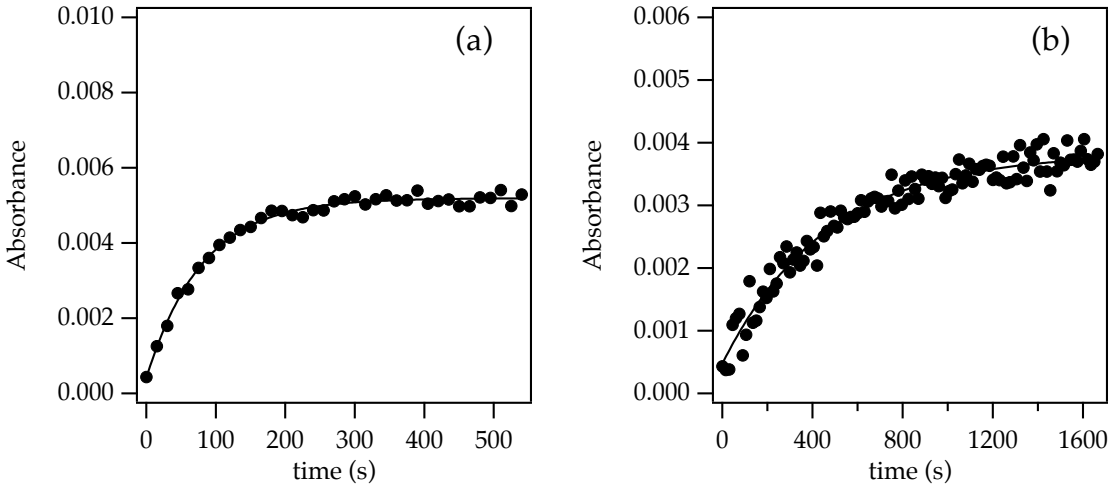


Figure A.1.54. IR spectra in $CHCl_3$ recorded at 0 °C: (a) injecting 0.002 M **1** into pre-mixed 0.040 M Bu_2BOTf and 0.080 M *i*-Bu_3N, following growth of **4**, k_{obsd} = 0.02 s^{-1}; (b) injecting 0.002 M **1**-***d***$_2$ into pre-mixed 0.040 M Bu_2BOTf and 0.080 M *i*-Bu_3N, following growth of **4**-***d***, k_{obsd} = 0.002 s^{-1}. k_H/k_D = 10.

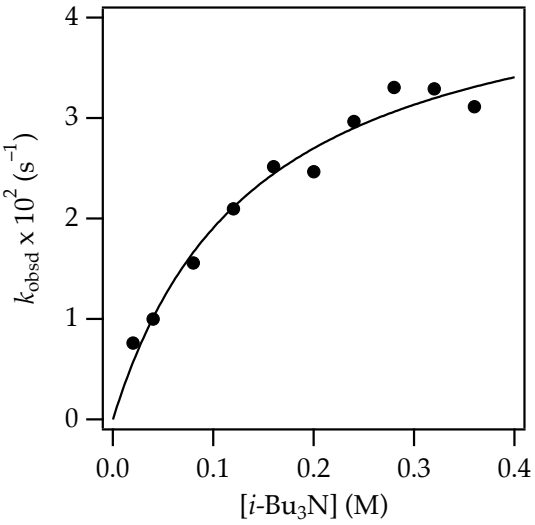


Figure A.1.55. Plot of observed rate vs added [*i*-Bu_3N] for enolization of **1** by Bu_2BOTf and *i*-Bu_3N in $CHCl_3$ at 0 °C. $y = ax / (x + b)$, $a = 0.046 \pm 0.004$, $b = 0.14 \pm 0.03$. K_{eq} = [**3**][*i*-Bu_3N] / [**1**][*i*-$Bu_3N{\cdot}Bu_2BOTf$] = b / [*i*-$Bu_3N{\cdot}Bu_2BOTf$] = 3.5

[**1**] (M)	[*i*-$Bu_3N{\cdot}Bu_2BOTf$] (M)	[*i*-Bu_3N] (M)	k_{obsd} x 10^2 (s^{-1})
0.0020	0.040	0.020	0.762
0.0020	0.040	0.040	1.00
0.0020	0.040	0.080	1.56
0.0020	0.040	0.12	2.10
0.0020	0.040	0.16	2.55
0.0020	0.040	0.20	2.47
0.0020	0.040	0.24	2.97
0.0020	0.040	0.28	3.30
0.0020	0.040	0.32	3.29
0.0020	0.040	0.36	3.11

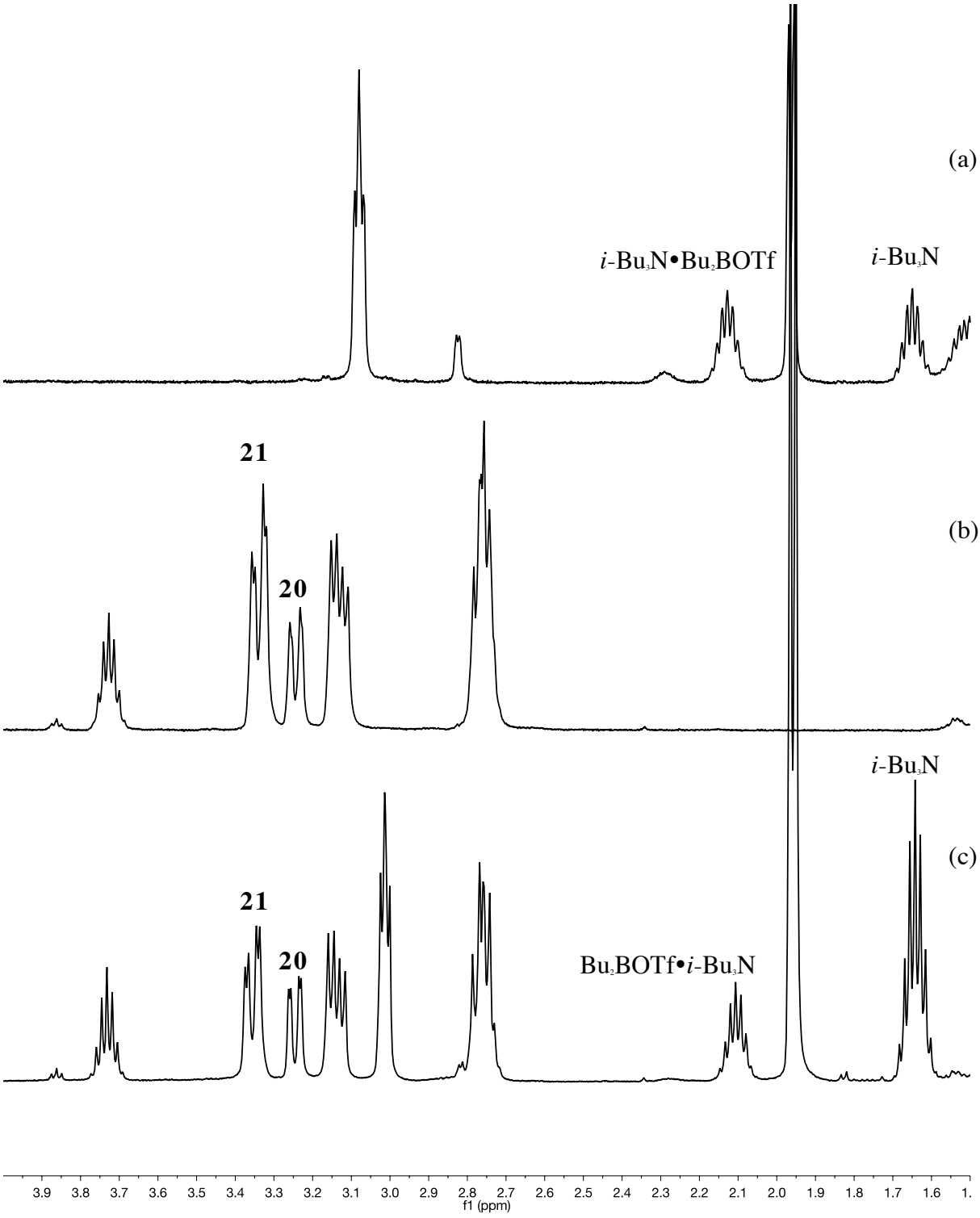


Figure A.1.56. ^{1}H NMR spectra in $CDCl_3$ at 0 °C: (a) 0.10 M Bu_2BOTf and 0.03 M *i*-Bu_3N; (b) 0.10 M Bu_2BOTf, and 0.10 M **20**; (c) 0.10 M Bu_2BOTf, 0.05 M *i*-Bu_3N, and 0.10 M **20**.

K_{eq} = [**21**][*i*-Bu_3N] / [**20**][*i*-Bu_3N□Bu_2BOTf] = 4.

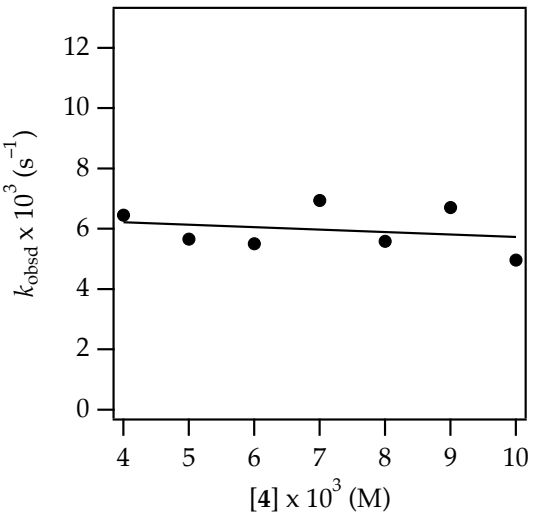


Figure A.1.57. Plot of observed rate vs [**4**] for aldol reaction of **4** and *i*-PrCHO in $CHCl_3$ at –60 °C. $y = ax + b$, $a = -0.1 \pm 0.1$, $b = 0.006 \pm 0.001$.

[**4**] (M)	[*i*-PrCHO] (M)	k_{obsd} x 10^3 (s^{-1})
0.0040	0.10	6.46
0.0050	0.10	5.66
0.0060	0.10	4.89
0.0070	0.10	6.94
0.0080	0.10	4.61
0.0090	0.10	6.71
0.010	0.10	4.97

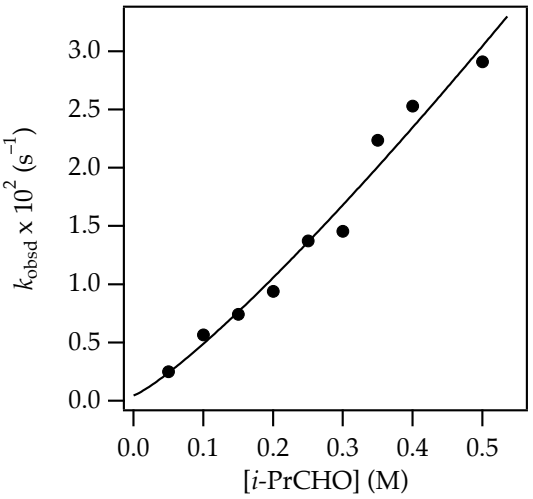


Figure A.1.58. Plot of observed rate vs [*i*-PrCHO] for aldol reaction of **4** and *i*-PrCHO in $CHCl_3$ at –60 °C. $y = ax^b + c$, $a = 0.067 \pm 0.007$, b = 1.09 ± 0.10, c set to 0.00.

[**4**] (M)	[*i*-PrCHO] (M)	k_{obsd} x 10^2 (s^{-1})
0.0050	0.050	0.250
0.0050	0.10	0.566
0.0050	0.15	0.742
0.0050	0.20	0.940
0.0050	0.25	1.37
0.0050	0.30	1.45
0.0050	0.35	2.24
0.0050	0.40	2.53
0.0050	0.50	2.91

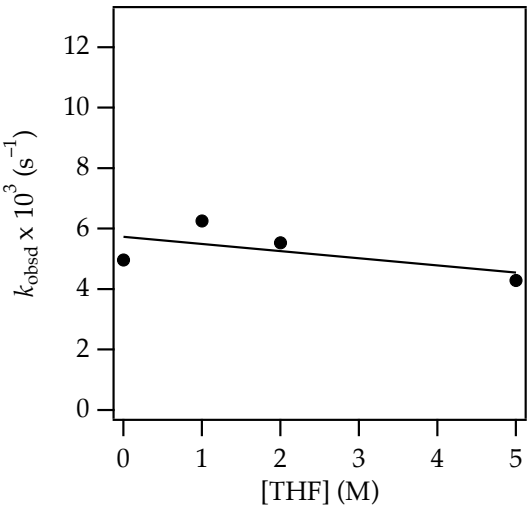


Figure A.1.59. Plot of observed rate vs added [THF] for aldol reaction of **4** and *i*-PrCHO in $CHCl_3$ at –60 °C. $y = ax + b$, $a = -0.0002 \pm 0.0002$, $b = 0.0057 \pm 0.0006$.

[**4**] (M)	[*i*-PrCHO] (M)	[THF] (M)	k_{obsd} x 10^3 (s^{-1})
0.0050	0.10	0	4.9691
0.0050	0.10	1.0	6.2526
0.0050	0.10	2.0	5.5373
0.0050	0.10	5.0	4.2908

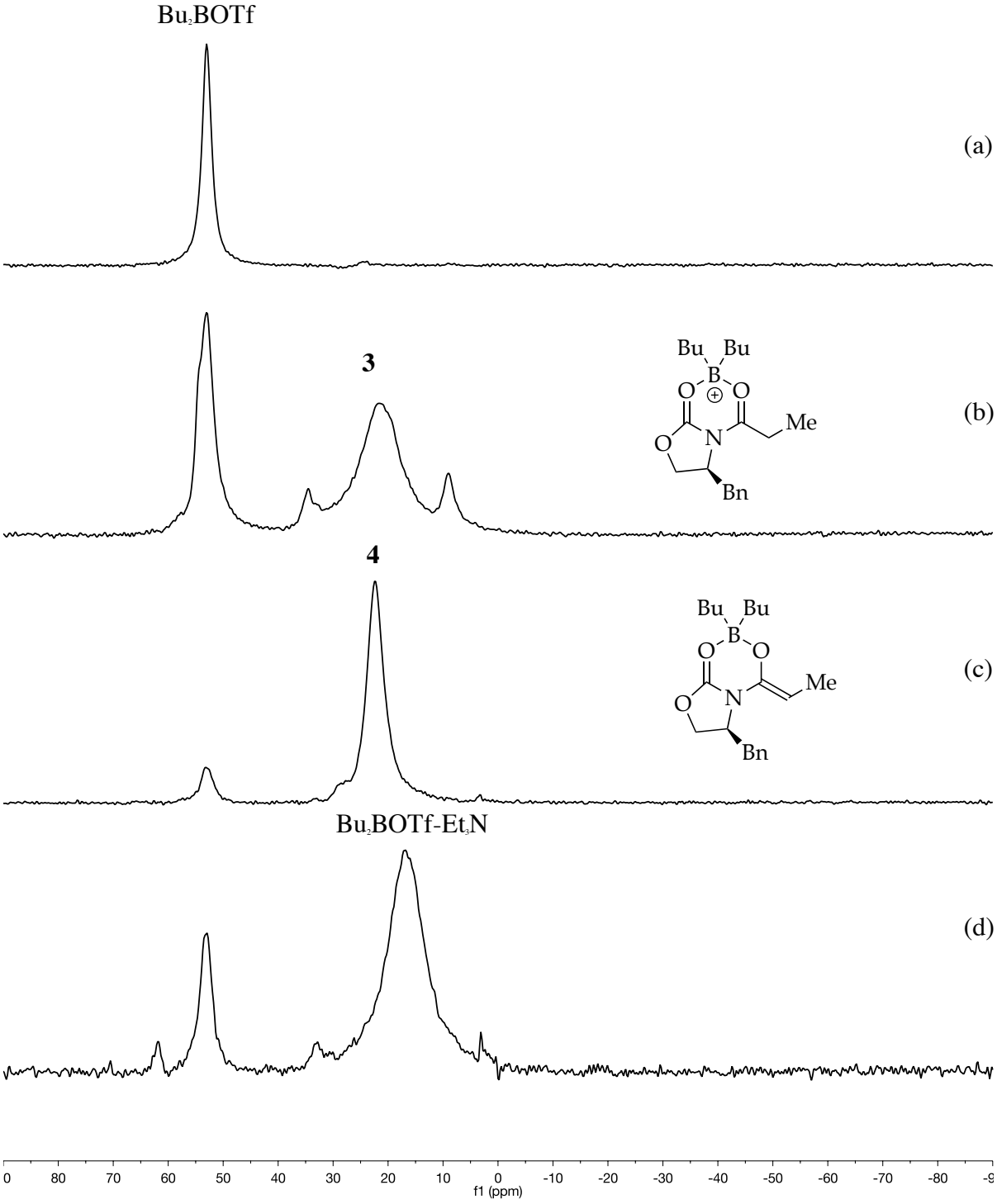


Figure A.1.60. ^{11}B NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.10 M Bu_2BOTf and 0.10 M **1**; (c) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **1**; (d) 0.10 M Bu_2BOTf and 0.10 M Et_3N.

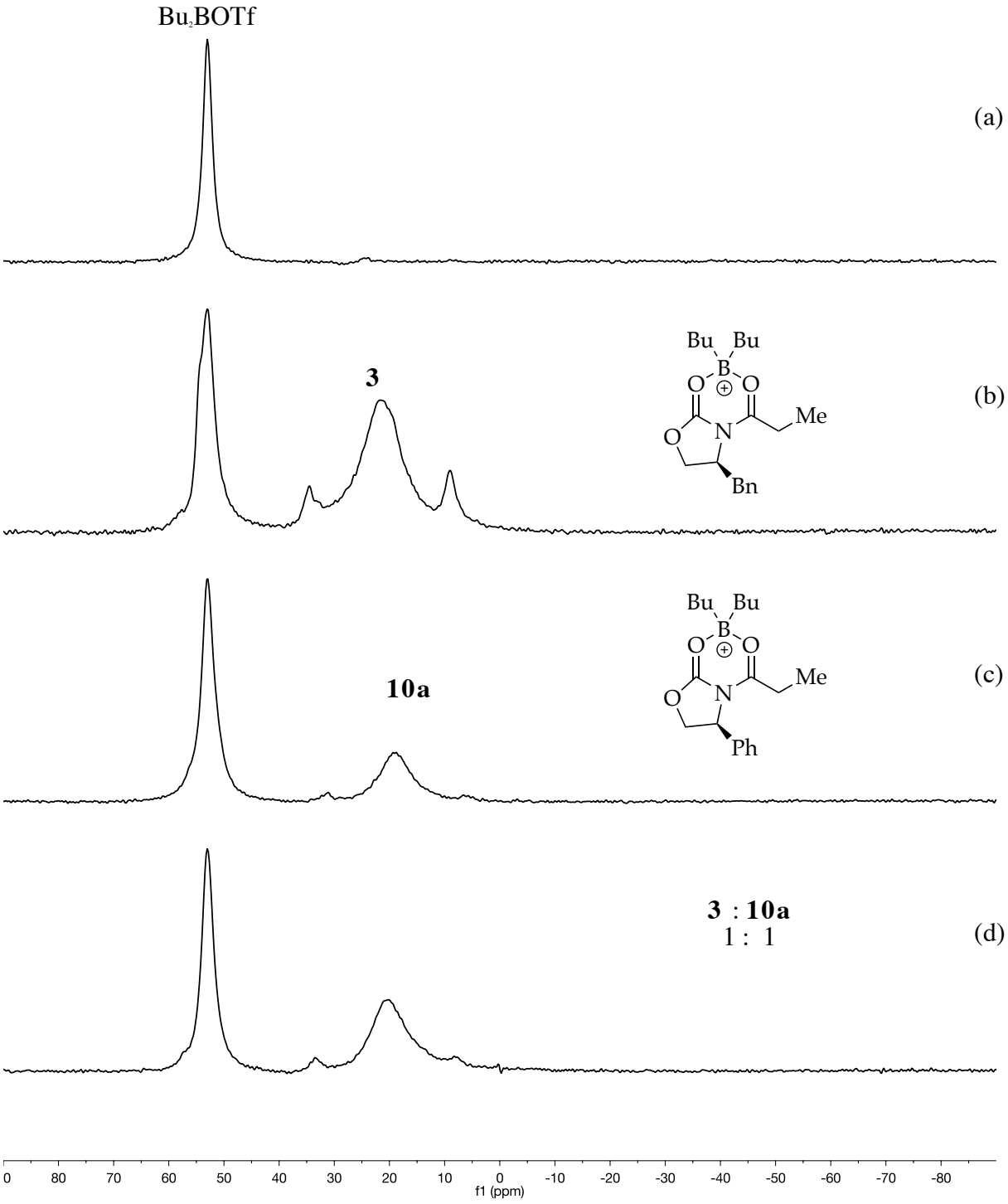


Figure A.1.61. ^{11}B NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.11 M Bu_2BOTf and 0.10 M **1**; (c) 0.11 M Bu_2BOTf and 0.10 M **10**; (d) 0.11 M Bu_2BOTf, 0.050 M **1** and 0.050 M **10**.

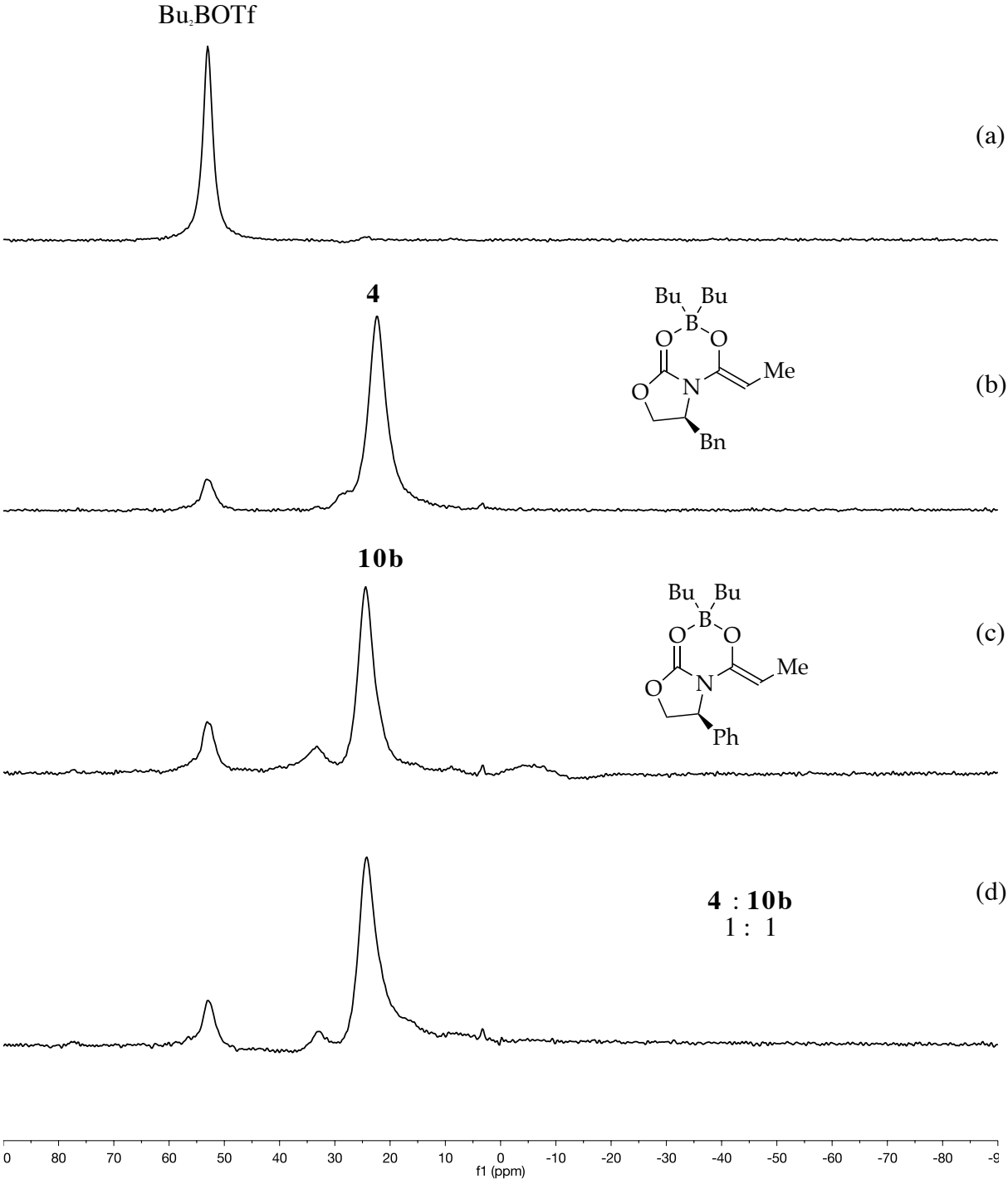


Figure A.1.62. ^{11}B NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **1**; (c) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **10**; (d) 0.10 M Bu_2BOTf, 0.10 M Et_3N, 0.050 M **1**, and 0.050 M **10**.

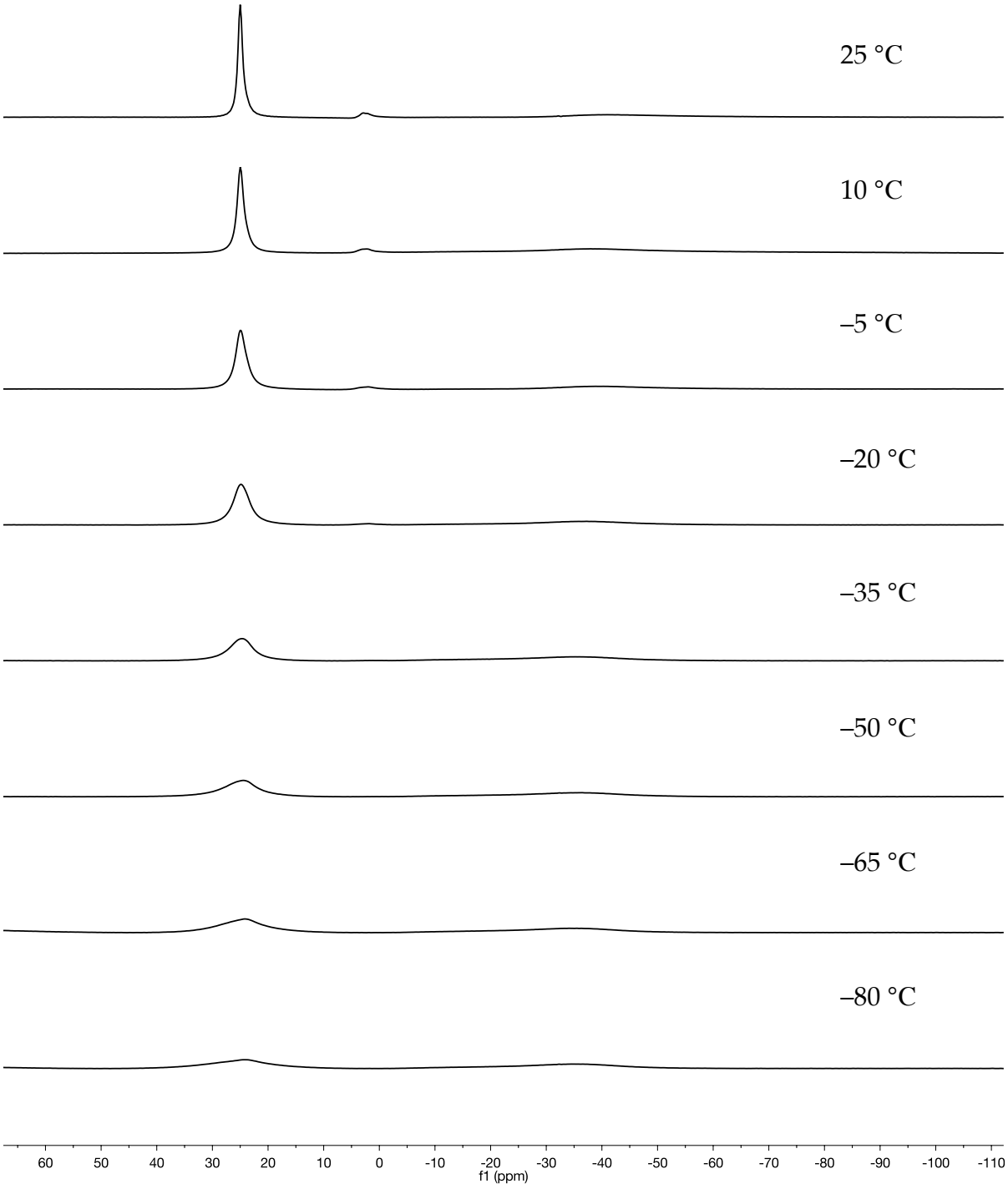


Figure A.1.63. ^{11}B NMR spectra of 0.05 M **1**, 0.05 M **10**, 0.10 M Bu_2BOTf, and 0.10 M Et_3N in CH_2Cl_2 recorded at: (a) 25 °C; (b) 10 °C; (c) –5 °C; (d) –20 °C; (e) –35 °C; (f) –50 °C; (g) –65 °C; (h) –80 °C.

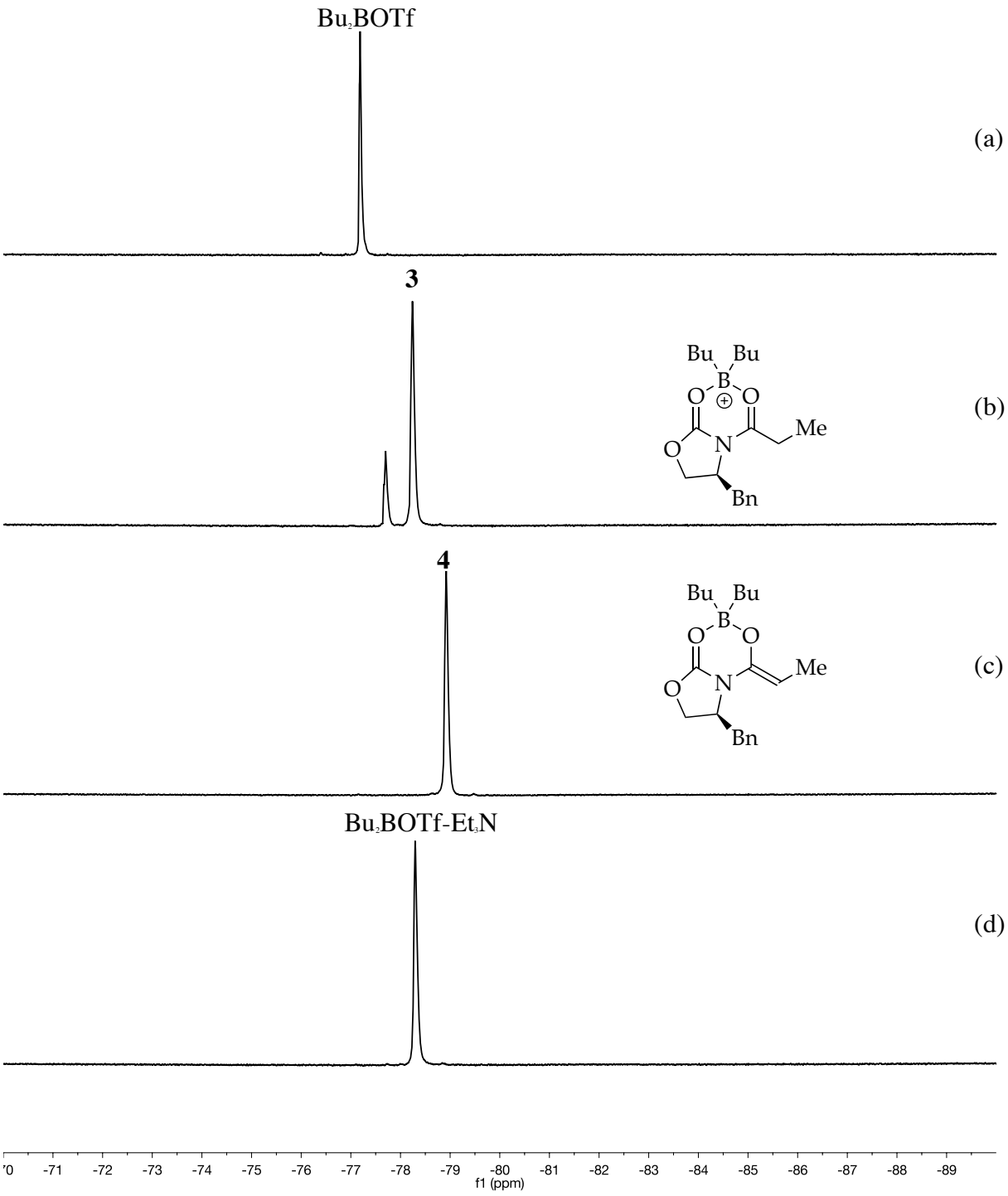


Figure A.1.64. ^{19}F NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.10 M Bu_2BOTf and 0.10 M **1**; (c) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **1**; (d) 0.10 M Bu_2BOTf and 0.10 M Et_3N in $CHCl_3$.

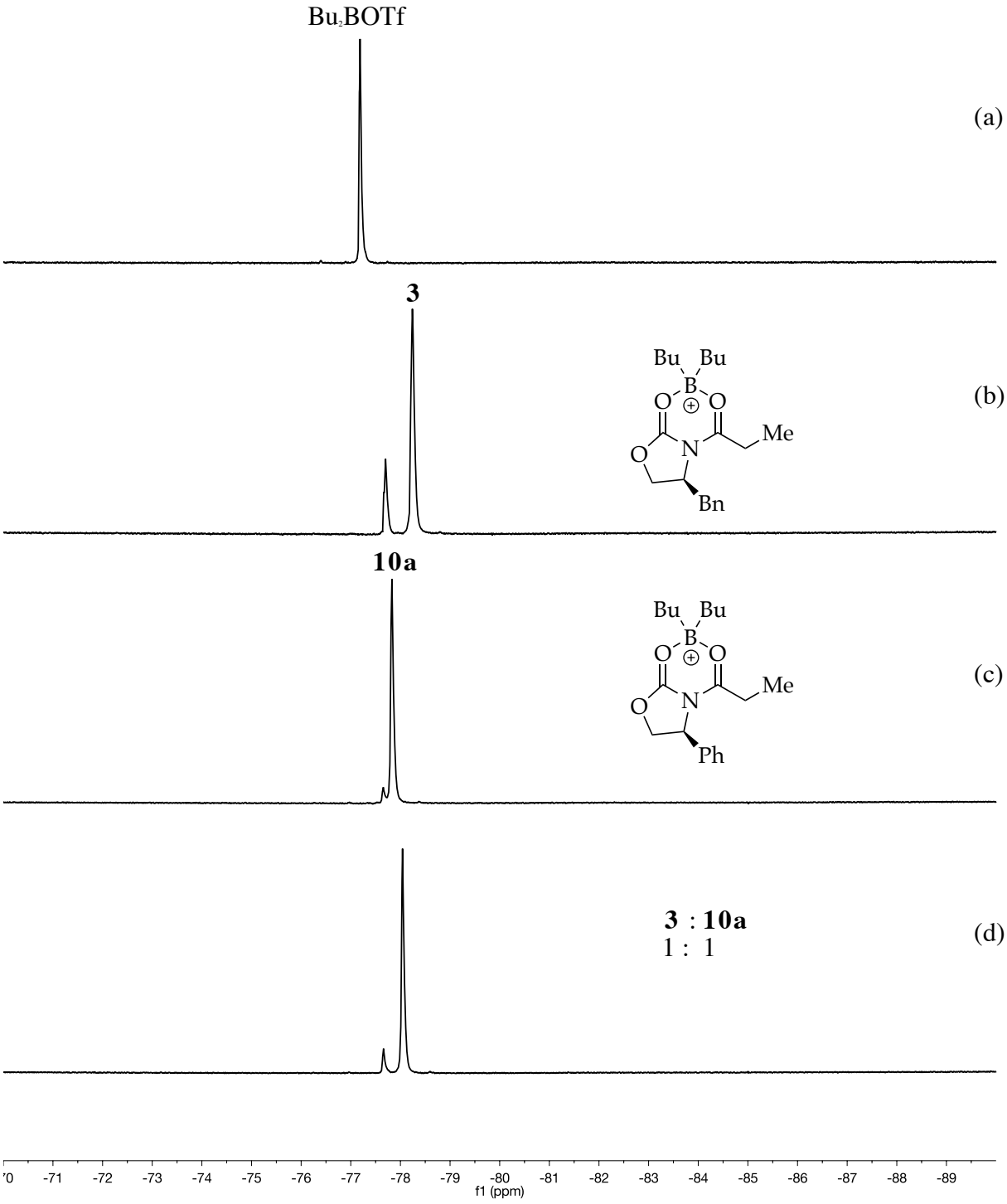


Figure A.1.65. ^{19}F NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.10 M Bu_2BOTf and 0.10 M **1**; (c) 0.10 M Bu_2BOTf and 0.10 M **10**; (d) 0.10 M Bu_2BOTf, 0.050 M **1**, and 0.050 M **10**.

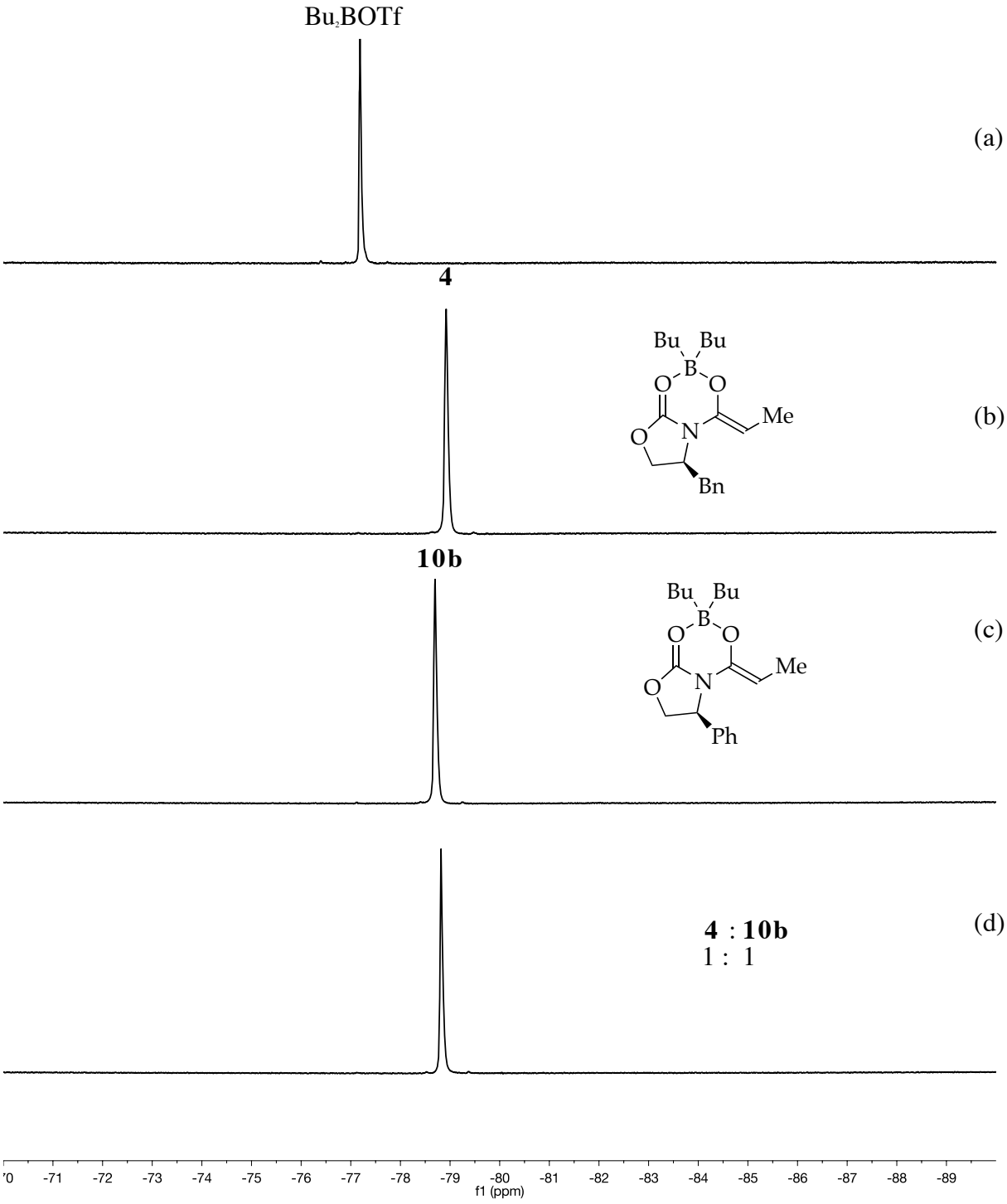


Figure A.1.66. ^{19}F NMR spectra in $CHCl_3$ at rt: (a) 0.10 M Bu_2BOTf; (b) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **1**; (c) 0.10 M Bu_2BOTf, 0.10 M Et_3N, and 0.10 M **10**; (d) 0.10 M Bu_2BOTf, 0.10 M Et_3N, 0.050 M **1**, and 0.050 M **10**.

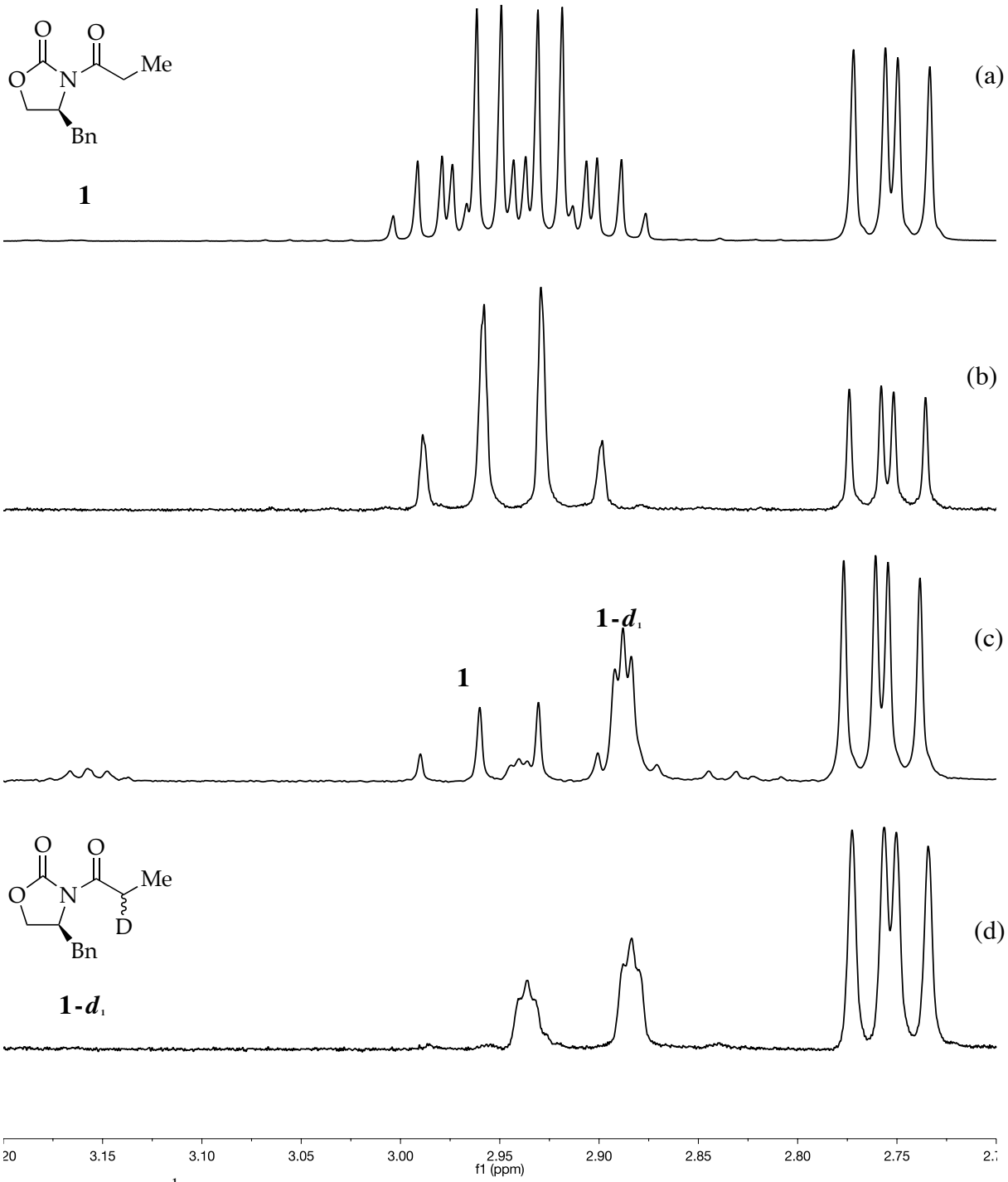
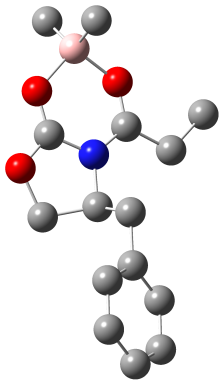
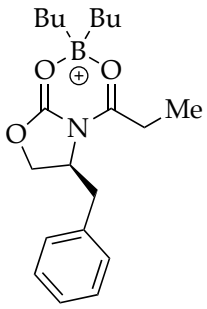


Figure A.1.67. ^{1}H NMR spectra in $CDCl_3$ at rt: (a) 0.10 M **1**; (b) 0.10 M **1** single frequency irradiated at 1.2 ppm; (c) 0.10 M **1**-d_1 single frequency irradiated at 1.2 ppm, **1**-d_1 prepared by enolizing **1** and quenching with MeOD; (c) 0.10 M **1**-d_1 single frequency irradiated at 1.2 ppm, **1**-d_1 prepared by enolizing **1**-d_2 and quenching with MeOH.

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). GMP2 is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table A.1.1. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **3** at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).



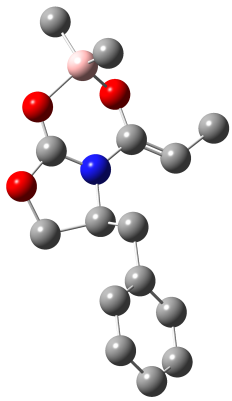


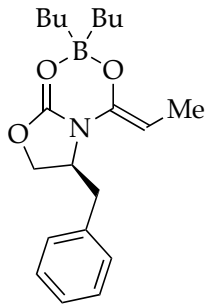
G = –889.064536
G_{MP2} = –886.2253287

C	0.00000000	0.00000000	0.00000000	C	–0.48732100	–1.41496800	0.10895100
N	0.38016100	–2.45702000	–0.11871500	C	–0.09693500	–3.75911200	–0.20012400
O	0.82970100	–4.58525800	–0.59899000	C	2.02567500	–3.83066600	–0.99729600
H	2.89179500	–4.38173500	–0.63593600	H	2.02451800	–3.79413300	–2.08831300
C	1.85930100	–2.44914500	–0.32849800	H	2.12408400	–1.64921500	–1.02250300
C	2.63961200	–2.30806200	0.99696700	H	2.34630000	–1.37073100	1.48433900
H	2.34344500	–3.12190000	1.66979600	C	4.13676100	–2.33617400	0.75902500
C	4.78360800	–1.23720700	0.17527300	C	6.15628700	–1.26957800	–0.06703000
C	6.90027700	–2.40224400	0.27289700	C	6.26759300	–3.49843700	0.85973800
C	4.89241100	–3.46555200	1.10074600	H	4.41038900	–4.31565800	1.57940900
H	6.84253200	–4.37652300	1.13824200	H	7.97005900	–2.42528800	0.08856600
H	6.64654100	–0.40897800	–0.51236400	H	4.21817600	–0.34119500	–0.07573700
O	–1.25525800	–4.11170100	0.04809200	B	–2.38877500	–3.08719400	0.63632600
O	–1.68344800	–1.66079400	0.37005600	C	–2.46566600	–3.30024300	2.20259600
H	–3.16510700	–2.58742400	2.65558100	H	–2.84581100	–4.30358300	2.42963800
H	–1.50446200	–3.19106700	2.72326000	C	–3.64863000	–3.19126100	–0.30729400
H	–4.41721000	–2.46892900	–0.00724700	H	–3.42381000	–3.01374200	–1.36633400

H	–4.10161800	–4.18689100	–0.23100800	H	0.84143800	0.12081500	0.69556400
H	0.42965100	0.12207400	–1.00530000	C	–1.08580800	1.04576800	0.26525000
H	–1.49450700	0.94735800	1.27407500	H	–0.65211700	2.04380500	0.16583600
H	–1.90830400	0.95510600	–0.44839600				

Table A.1.2. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **4** at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).





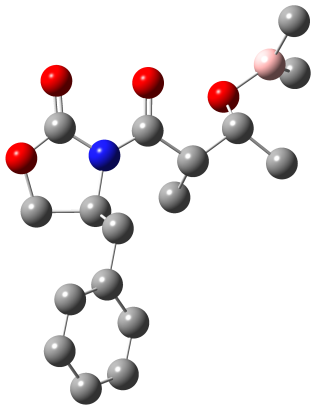
G = –888.683863

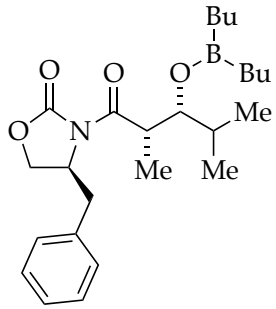
G_{MP2} = –885.8517903

C	0.00000000	0.00000000	0.00000000	H	0.86194600	–0.55053500	0.37634100
H	0.01345200	0.00976800	–1.09379900	C	–0.14084700	1.41226200	0.60276500
H	0.16546300	2.17521000	–0.11782500	C	0.61447000	1.60492700	1.93914000
H	0.26852700	2.54210700	2.38764200	H	0.32010900	0.79881800	2.62191700
C	2.11725700	1.61928000	1.75816500	C	2.75673300	2.73175300	1.19066000
C	4.13729100	2.74040100	0.99477300	C	4.90509700	1.63394600	1.36573800
C	4.28311000	0.52318600	1.93596200	C	2.89998600	0.51779800	2.12923800
H	2.42426100	–0.34640400	2.58822300	H	4.87276800	–0.33878400	2.23617300
H	5.98125200	1.64148400	1.21669500	H	4.61491500	3.61354900	0.55845700
H	2.17017300	3.60467200	0.91063600	N	–1.59755100	1.45758700	0.78049100
C	–2.11284100	0.21244300	0.76572400	O	–1.19809100	–0.70368800	0.42389200
O	–3.27853100	–0.12083700	1.04827000	B	–4.22791400	1.09766000	1.72922100
O	–3.71868600	2.32173200	1.04747100	C	–2.42492900	2.61558900	0.97813700
C	–1.90445800	3.85546700	0.99084200	H	–0.83758200	3.98140000	0.83625400
C	–2.73962600	5.08872000	1.17369100	H	–2.38226500	5.69353000	2.01823100
H	–2.70883200	5.73440100	0.28481000	H	–3.78271400	4.82299900	1.36061400

C	–3.88860100	1.03585000	3.29955100	H	–2.83148200	1.22726000	3.53786100
H	–4.47126200	1.79557300	3.83807900	H	–4.14974800	0.06399300	3.73727800
C	–5.71782500	0.78280600	1.25521300	H	–6.41363400	1.53470600	1.65126700
H	–5.81954500	0.79223300	0.16234300	H	–6.06358500	–0.19472000	1.61472200

Table A.1.3. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **6** at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).



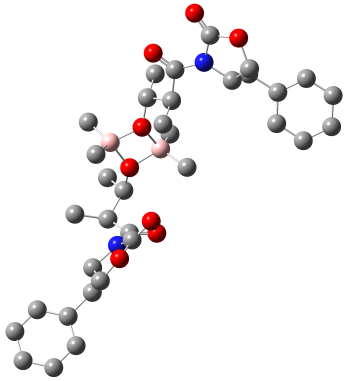


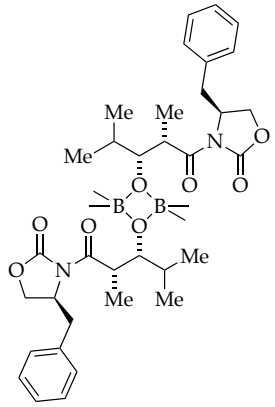
G = –1042.491306
G_{MP2} = –1039.186804

C	0.00000000	0.00000000	0.00000000	C	0.06915800	1.46054400	–0.46807000
N	1.30876700	2.11094400	–0.28573900	C	1.48947800	3.50414400	–0.48621800
O	2.76919300	3.81322000	–0.10796700	C	3.37166200	2.68777900	0.54621800
H	4.43538600	2.67399700	0.30535600	H	3.24322800	2.79442800	1.62972000
C	2.60730800	1.47594800	–0.00349700	H	2.51008900	0.70362000	0.76152800
C	3.25000700	0.88215300	–1.28220600	H	2.53739800	0.18232400	–1.73515900
H	3.39145900	1.69563000	–2.00346100	C	4.56517400	0.18283800	–1.01050900
C	4.58811300	–1.08195200	–0.40399900	C	5.79571700	–1.72108100	–0.12515600
C	7.00599700	–1.10450200	–0.45070400	C	6.99823900	0.15083800	–1.05913800
C	5.78660700	0.78768900	–1.33588700	H	5.78883200	1.76102500	–1.82177100
H	7.93427300	0.63502300	–1.32404500	H	7.94746700	–1.60271300	–0.23663900
H	5.79217300	–2.70284200	0.34080500	H	3.65076100	–1.57727100	–0.15704000
O	0.71598700	4.31475500	–0.90533900	O	–0.89593100	2.04448300	–0.91415100
H	0.93252000	–0.50992700	–0.26964100	C	–1.14146400	–0.74982300	–0.73502000
H	–1.14844900	–0.41600400	–1.77783400	C	–0.95144200	–2.26732100	–0.69811800
H	–1.76965200	–2.75673300	–1.23595700	H	–0.00783400	–2.55893100	–1.17412600

H	–0.95613400	–2.64310200	0.33036800	O	–2.38595500	–0.43657100	–0.11745000
B	–3.48556000	0.06750600	–0.76120500	C	–4.72066700	0.40330500	0.16714500
H	–4.98767800	1.46539800	0.06868000	H	–5.61250800	–0.15570900	–0.15020200
H	–4.54006200	0.19293600	1.22661700	C	–3.53355400	0.29834800	–2.32974900
H	–4.54326900	0.53583600	–2.68163400	H	–2.88615500	1.14629400	–2.59231400
H	–3.17469200	–0.56230600	–2.91073600	C	–0.15699100	–0.03881500	1.53578500
H	–1.07736300	0.46828300	1.83185300	H	–0.20974400	–1.07224000	1.89180300
H	0.68517200	0.44783100	2.03874700				

Table A.1.4. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **6** dimer at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).





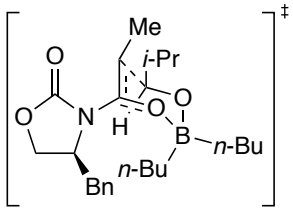
G = –2084.931299
G_{MP2} = –2078.355277

C	0.00000000	0.00000000	0.00000000	B	–0.18424700	–1.53080300	0.42597700
O	0.20300400	–2.55330800	–0.70750100	C	1.44412400	–3.06769100	–1.23151600
C	2.16192000	–1.96063300	–2.04084600	C	3.41604400	–2.55487100	–2.69367600
N	4.51433300	–1.69178400	–2.85493500	C	4.62469000	–0.29120200	–2.40790100
C	5.67602300	0.21093900	–3.40766900	H	6.33678400	0.97304900	–2.99332900
H	5.21715700	0.58420400	–4.33047600	O	6.45859700	–0.95343800	–3.71343100
C	5.71394900	–2.08233600	–3.50734000	O	6.07763900	–3.17729400	–3.82420800
H	3.67960300	0.23753100	–2.54545400	C	5.09092300	–0.18355200	–0.93517200
H	4.38104600	–0.73339300	–0.30592500	H	6.05512700	–0.69749000	–0.84355200
C	5.21251800	1.24955200	–0.45979000	C	6.46857300	1.84986700	–0.29920800
C	6.58066400	3.17967700	0.11207300	C	5.43355700	3.93093100	0.36866200

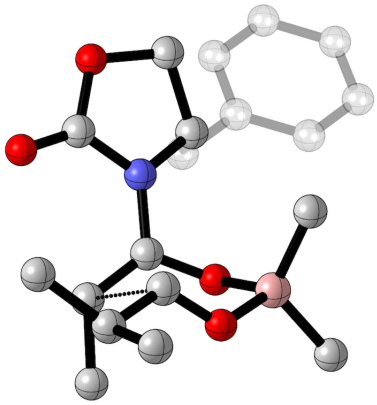
C	4.17548300	3.34357700	0.21640400	C	4.06729300	2.01484100	–0.19309300
H	3.08059400	1.56767600	–0.29712200	H	3.27628100	3.91816100	0.42150200
H	5.51787300	4.96541500	0.69018200	H	7.56440600	3.62494600	0.23454400
H	7.36767800	1.26692000	–0.48747700	O	3.42549400	–3.69345700	–3.11764300
H	2.42377000	–1.15705600	–1.34659500	C	1.28241800	–1.38478700	–3.17170700
H	0.36268200	–0.95656400	–2.77119300	H	1.81094300	–0.59857400	–3.72257000
H	1.02267500	–2.17338200	–3.88527500	H	1.15765800	–3.85769400	–1.92959600
C	2.31277900	–3.67103800	–0.12836300	H	2.68985100	–2.90461600	0.55627500
H	1.73740300	–4.39438800	0.45477600	H	3.16221900	–4.19327100	–0.57627000
B	–1.20376300	–3.23723400	–0.80804700	O	–1.66668900	–2.06149700	0.17140800
C	–2.74904200	–1.83439500	1.09640500	H	–2.44941700	–0.93492400	1.63721200
C	–2.93610200	–2.97027500	2.10242500	H	–3.19886100	–3.91863800	1.62984000
H	–2.01695600	–3.12171400	2.67172700	H	–3.73255600	–2.70435200	2.80760400
C	–4.06994200	–1.45516700	0.36073700	H	–4.74813500	–1.17743100	1.18218700
C	–4.71754100	–2.59969500	–0.42934000	H	–5.78404700	–2.42288100	–0.59219600
H	–4.23977100	–2.74421100	–1.39871200	H	–4.64174900	–3.53885400	0.12434800
C	–3.81522000	–0.14309500	–0.41059200	O	–3.11886800	0.72710600	0.06171800
N	–4.37596800	0.02953000	–1.71030000	C	–5.78156800	–0.14699400	–2.11525500
C	–5.81576900	0.74638600	–3.37548800	H	–6.37113500	0.29790700	–4.20010900
H	–6.23390800	1.73580100	–3.15690000	O	–4.45066300	0.90278800	–3.77830900
C	–3.61697000	0.61490400	–2.73908900	O	–2.42847100	0.78638300	–2.77986300
H	–5.97144700	–1.18894500	–2.39438300	C	–6.80046600	0.29633300	–1.04716600
H	–6.68127600	–0.32585600	–0.15212900	H	–6.56611800	1.32574800	–0.75180800
C	–8.23045900	0.20356700	–1.54335200	C	–8.85433000	–1.04363900	–1.69678400
C	–10.1611100	–1.13621500	–2.17464300	C	–10.8698840	0.02097700	–2.50510600
C	–10.2637160	1.26789700	–2.35114700	C	–8.95446900	1.35649300	–1.87389600
H	–8.49406000	2.33359500	–1.74582300	H	–10.8096150	2.17446400	–2.59787100
H	–11.8892210	–0.04963700	–2.87428500	H	–10.6279940	–2.11144100	–2.28319500
H	–8.31701800	–1.95175400	–1.43041000	C	–1.78316100	–3.10618800	–2.29884400
H	–1.95920400	–2.06787400	–2.60535900	H	–1.06155100	–3.52920900	–3.01257300
H	–2.70784500	–3.67618200	–2.45437200	C	–1.22600200	–4.70924300	–0.16605200
H	–0.62205400	–5.39158700	–0.78175000	H	–0.83712300	–4.76842200	0.85736500
H	–2.23707900	–5.13872000	–0.16198300	C	0.36254000	–1.91099400	1.89117700
H	1.40220500	–1.58269700	2.02242400	H	–0.20807300	–1.37559600	2.66381300
H	0.32613400	–2.97911100	2.13691600	H	–0.45234700	0.25595000	–0.96320100
H	–0.45040600	0.66988400	0.74353700	H	1.06752800	0.26656300	–0.03716700

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). GMP2 is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table A.1.5. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **5a** at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).



5

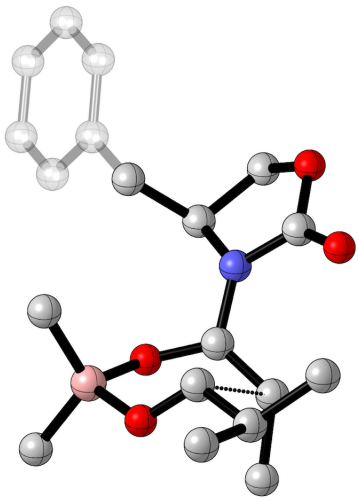


G = –1121.025373
G_{MP2} = –1117.4267

C	0.00000000	0.00000000	0.00000000	N	1.35954500	0.39397900	0.40479600
C	2.17546600	-0.46286400	1.18951100	C	3.20126000	-0.00479200	1.97501300
H	3.33829400	1.06690800	2.03864900	C	3.90854100	-0.87643100	2.97353800
H	3.95071000	-1.92044700	2.65555500	H	3.38884900	-0.84759400	3.94184900
H	4.92933500	-0.51966800	3.15581300	O	1.88995200	-1.74484200	1.06504100
B	2.60353000	-2.63926500	0.01775100	O	4.10334500	-2.13400800	0.13753500
C	4.40294200	-0.92231500	-0.07898300	C	5.80903000	-0.44301100	0.16292700
H	6.07452200	-0.70364200	1.19477400	C	6.75689700	-1.23646300	-0.77015500
H	7.79184600	-0.92852600	-0.58748700	H	6.52911200	-1.04140700	-1.82472400
H	6.67308000	-2.31175800	-0.59134000	C	5.93805500	1.07010400	-0.05289700
H	5.77020300	1.32956600	-1.10551900	H	6.94609400	1.40530100	0.21189700
H	5.21516100	1.63234500	0.54450300	H	3.76054600	-0.32202200	-0.73014500
C	2.08662900	-2.40680600	-1.49579600	H	2.68907200	-2.99314900	-2.20279700
H	1.05411300	-2.76542300	-1.60615700	H	2.10018100	-1.36729900	-1.85380400
C	2.57357000	-4.14894100	0.54648000	H	3.00484300	-4.25176000	1.55086900
H	1.54307600	-4.52520200	0.59880400	H	3.12478100	-4.82534200	-0.12022000

C	1.57111700	1.75054800	0.17819000	O	0.51577100	2.24485000	-0.52597000
C	-0.33053700	1.15906700	-0.95209700	H	-1.36904800	1.48694700	-0.88961400
H	-0.08697300	0.91849400	-1.99287200	O	2.51583100	2.43095800	0.50861700
C	-0.95249300	-0.11605100	1.21362200	H	-0.50238900	-0.82263700	1.91930200
H	-1.00860300	0.85826100	1.71471000	C	-2.33529100	-0.58686700	0.81775500
C	-3.41568900	0.30290100	0.75293000	C	-4.68194900	-0.13384600	0.35738800
C	-4.88604800	-1.47182600	0.01951600	C	-3.81821100	-2.37034400	0.08375300
C	-2.55561500	-1.93098700	0.48032000	H	-1.73114200	-2.63856000	0.53875800
H	-3.97018000	-3.41614100	-0.17001000	H	-5.87076700	-1.81449400	-0.28653200
H	-5.50796800	0.57141100	0.31827200	H	-3.26726900	1.34536400	1.02719200
H	0.02936600	-0.94941400	-0.53278900				

Table A.1.6. Optimized geometries at B3LYP level of theory with 6–31G(d) basis set for **5b** at –78 °C with free energies (Hartrees) and Cartesian coordinates (X, Y, Z) (Note: GMP2 includes single point MP2 corrections to B3LYP/6–31G(d) optimized structures).



G = –1121.019933

G_{MP2} = –1117.419194

B	0.00000000	0.00000000	0.00000000	C	0.67192100	-0.07062900	-1.46619200
H	1.67706900	-0.50908600	-1.41753400	H	0.08412700	-0.72633900	-2.12313600
H	0.77150400	0.89472800	-1.98242900	C	-0.14606500	-1.39629700	0.77088600
H	-0.68060200	-2.14045500	0.16554800	H	0.84267400	-1.81906400	0.99355500
H	-0.67834000	-1.30832600	1.72741700	O	-1.46059400	0.59314900	-0.16816800
C	-1.65175800	1.78077700	-0.55368100	H	-0.86048300	2.30846300	-1.09387100
C	-3.05081000	2.32651200	-0.61795600	H	-3.51910500	2.13787700	0.35629500

C	-3.07363100	3.82556200	-0.93850300
H	-2.68319000	4.01554700	-1.94555600
C	-3.83529800	1.50359500	-1.67134900
H	-4.87045100	1.85846100	-1.71194500
O	0.70311000	1.01731400	0.93923400
N	1.35750900	3.18746500	0.53038400
O	0.05367200	5.01323800	-0.13126500
C	3.31604600	4.37813200	0.73890200
H	3.01081700	2.36843200	1.55073700
H	2.82189900	1.23613500	-0.67708800
C	4.86083400	1.87715800	-0.42790500
C	6.65960400	0.61194800	0.61515500
C	7.18595400	2.34475400	-0.97883100
H	5.50206500	3.37442000	-1.83964100
H	8.66772500	1.14288900	0.02766400
H	4.56721000	0.28586700	0.99864800
H	3.40978600	4.71274300	1.77842100
H	-0.87584000	3.82928300	1.72713700
H	-2.70322900	2.16208500	2.39293400
H	-1.42360300	2.09918400	3.59674800
H	-2.46373300	4.40194700	-0.23954000
H	-4.10218600	4.19963900	-0.90556400
H	-3.83747700	0.43990200	-1.41843700
H	-3.39968800	1.62255600	-2.67031400
C	0.38721800	2.28933000	1.06687500
C	1.11320300	4.49961800	0.14844800
O	2.29913400	5.16945500	0.09345500
C	2.80627200	2.92979200	0.63552200
C	3.38213700	2.16705100	-0.57663900
H	3.19814000	2.75902100	-1.48183600
C	5.29995100	0.87384900	0.44963600
C	7.60820500	1.34879100	-0.09806700
C	5.82323500	2.60499000	-1.14042800
H	7.91533900	2.91786600	-1.54526300
H	6.97885500	-0.17260400	1.29623100
H	4.25984000	4.54252300	0.21801800
C	-0.74654100	2.75419200	1.67710500
C	-1.64413500	1.91140200	2.53611000
H	-1.51156000	0.84414800	2.35479300

Chapter 1 References and Footnotes

1. (a) Evans, D. A.; Shaw, J. T. *L'actualité Chimique* **2003**, 35. (b) Lin, G.-Q.; Li, Y.-M.; Chan, A. S. C. *Principles and Applications of Asymmetric Synthesis*, Wiley & Sons: New York, 2001; 135. (c) Modern Aldol Reactions, Vols. 1 and 2 (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, 2004.

2. Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

3. The term "triflate" derives from the University of California, Berkeley and was cinematically inspired by science fiction movie, *The Day of the Triffids*. Charles Wilkins, personal communication.

4. (a) Cowden, C. J. *Org. React*. **1997**, *51*, 1. (b) Abiko, A. In *Boron Reagents in Synthesis: ACS Symposium Series*; American Chemical Society: Washington, DC, p 123, 2016.

5. Evans, D. A.; Kim, A. S.; Skrydstrup, T.; Taaning, R. H. *(S)-4-Benzyl-2-oxazolidinone*; John Wiley & Sons, New York; p 1–18, 2007.

6. (a) Makino, Y.; Iseki, K.; Fujii, K.; Oishi, S.; Hirano, T.; Kobayashi, Y. *Tetrahedron Lett.* **1995**, *36*, 6527. (b) Shinasha, C. B.; Sunoj, R. B. *J. Am. Chem. Soc.* **2010**, *132*, 12319. (c) Sreenithya, A.; Sunoj, R. B. *Org. Lett.* **2012**, *14*, 5752. (d) Shinisha, C. B.; Sunoj, R. B. *Org. Lett.* **2010**, *12*, 2868.

7. Ma, L.; Hopson, R.; Li, D.; Zhang, Y.; Williard, P. G. *Organometallics* **2007**, *26*, 5834.

8. (a) Abiko, A.; Inoue, T.; Masamune, S. *J. Am. Chem. Soc.* **2002**, *124*, 10759. (b) Bai, J.; Burke, L. D.; Shea, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 4981.

9. For selected recent computational studies of boron enolates, see: (a) Dias, L. C.; Pinheiro, S. M.; Oliveira, V. M.; Ferreira, M. A. B.; Tormena, C. F.; Aguilar, A. M.; Zukerman-Schpector, J.; Tiekink, E. R. T. *Tetrahedron* **2009**, *65*, 8714. (b) Paton, R. S.; Goodman, J. M. *J. Org. Chem.* **2008**, *73*, 1253. (c) Dias, L. C.; de Lucca, Jr., E. C.; Ferreira, M. A. B.; Garcia, D. C.; Tormena, C. F. *J. Org. Chem.* **2012**, *77*, 1765. (d) Paton, R. S.; Goodman, J. M. *Org. Lett.* **2006**, *8*, 4299.

10. For a review of theoretical studies of boron enolates, see: Domingo, L. R.; Andres, J. In *The Chemistry of Metal Enolates*; Rappoport, Z., Ed.; Wiley: New York, 2009; Vol. 1, Chapter 1.

11. Cergol, K. M.; Jensen, P.; Turner, P.; Coster, M. J. *Chem. Commun.* **2007**, 1363.

12. (a) Tallmadge, E. H.; Collum, D. B. *J. Am. Chem. Soc.* **2015**, *137*, 13087. (b) Tallmadge, E. H.; Jermaks, J.; Collum, D. B. *J. Am. Chem. Soc.* **2016**, *138*, 345.

13. (a) Danda, H.; Hansen, M. M.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 173. (b) Baringhaus, K.-H.; Matter, H.; Kurz, M. *J. Org. Chem.* **2000**, *65*, 5031. (c) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099. (d) Kimball, D. B.; Michalczyk, R.; Moody, E.; Ollivault-Shiflett, M.; De Jesus, K.; Silks, L. A. III *J. Am. Chem. Soc.* **2003**, *125*, 14666.

14. Connolly, T. J.; Hansen, E. C.; MacEwan, M. F. *Org. Process Res. Dev.* **2010**, *14*, 466.

15. A copper complex of an acylated oxazolidinone shows similar IR absorbances: (a) Evans, D. A.; Scheidt, K. A.; Johnston, J. N.; Willis, M. C. *J. Am. Chem. Soc.* **2011**, *123*, 4480. (b) Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt, P. *J. Am. Chem. Soc.* **1999**, *121*, 7559.

16. For an excellent review of soft enolization, see: Evans, D. A.; Shaw, J. T. http://isites.harvard.edu/fs/docs/icb.topic93502.files/Lectures_and_Handouts/25-Handouts/SoftEnolization_draft.pdf

17. Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 11998.

18. Martin, N. H.; Allen, N. W. III; Moore, K. D.; Vo, L. *J. Molec. Struct. (Theochem)* **1998**, *454*, 161.

19. Evans invoked π stacking during oxazolidinone-derived enolate functionalizations: Evans, D. A.; Chapman, K. T.; Hung, D. T.; Kawaguchi, A. T. *Angew. Chem., Int. Ed.* **1987**, *26*, 1184.

20. Frisch, M. J.; *et al. GaussianVersion 3.09*; revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

21. Ma, Y.; Lobkovsky, E.; Collum, D. B. *J. Org. Chem.* **2005**, *70*, 2335.

22. For NMR spectroscopic studies of BF_3/R_3N complexes, see: Hartman, J. S.; Yuan, Z.; Fox, A.; Nguyen, A. *Can. J. Chem.* **1996**, *74*, 2131.

23. For a discussion and leading references to ligand substitutions of BR_3 derivatives, see: Toyota, S.; Futawaka, T.; Asakura, M.; Ikeda, H.; Oki, M. *Organometallics* **1998**, *17*, 4155.

24. For discussions of monitoring post-rate-limiting steps and the implications of rate limitation, see: (a) Simmons, E. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066. (b) Algera, R. F.; Gupta, L.; Hoepker, A. C.; Liang, J.; Ma, Y.; Singh, K. J.; Collum, D. B. *J. Org. Chem.* **2017**, *82*, 4513.

25. The rate law provides the stoichiometry of the transition structure relative to that of the reactants: (a) Edwards, J. O.; Greene, E. F.; Ross, J. *J. Chem. Educ.* **1968**, *45*, 381. (b) Collum, D. B.; McNeil, A. J.; Ramírez, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 3002.

26. (a) Vorontsova, L. G.; Chizhov, O. S.; Vasil'ev, L. S.; Mikhailov, B. M. *Izvest. Akad. Nauk. SSSR* **1981**, 353. (b) Gurskii, M. E.; Shashkov, A. S.; Mikhailov, B. M. *J. Organometal. Chem.* **1980**, *199*, 171.

27. Evans traced the need for excess Lewis acid in soft enolizations to ate complexes: (a) aluminum: Evans, D. A.; Allison, B. D.; Yang, M. G.; Masse, C. E. *J. Am. Chem. Soc.* **2001**, *123*, 10840. (b) boron: personal communication.

28. (a) Jordan, E.; Lestel, L.; Boileau, S.; Cheradame, H.; Gandini, A. *Makromolecular Chem.* **1989**, *190*, 267. (b) Papp, R.; Somoza, F. B.; Sieler. J.; Blaurock, S.; Hey-Hawkins, E. *J. Organometal. Chem.* **1999**, *585*, 127.

29. (a) Miyamoto, K.; Yokota, Y.; Suefuji, T.; Yamaguchi, K.; Ozawa, T.; Ochiai, M. *Chem.–Eur. J.* **2014**, *20*, 5447. (b) Uruichi, M.; Yakushi, K.; Yamashita, Y. *J. Materials Chem.* **2000**, *10*, 2716. (c) Chaudhuri, M. K.; Das, B. *Inorg. Chem.* **1985**, *24*, 2580. (d) Brownstein, S. *Can. J. Chem.* **1967**, *45*, 2403. (e) Koner, S.; Ghosh, A.; Chaudhuri, N. R. *Bull. Chem. Soc. Japan* **1990**, *63*, 2387.

30. Aubrecht, K. B.; Winemiller, M. D.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 11084.

31. Oxazolidinones: (a) **8**: Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *Tetrahedron* **1988**, *44*, 5525. (b) **11**: Perry, M. A.; Trinidad, J. V.; Rychnovsky, S. D. *Org. Lett.* **2013**, *15*, 472. (c) **12**: Szostak, M.; Spain, M.; Eberhart, A. J.; Procter, D. J. *J. Am. Chem. Soc.* **2014**, *36*, 2268. (d) **13**: Evans, D. A.; Mathre, D. J.; Scott, W. L. *J. Org. Chem.* **1985**, *50*, 1830.

CHAPTER 2

STRUCTURES AND REACTIVITIES OF SODIATED EVANS ENOLATES: ROLE OF SOLVATION AND MIXED AGGREGATION ON THE STEREOCHEMISTRY AND MECHANISM OF ALKYLATIONS

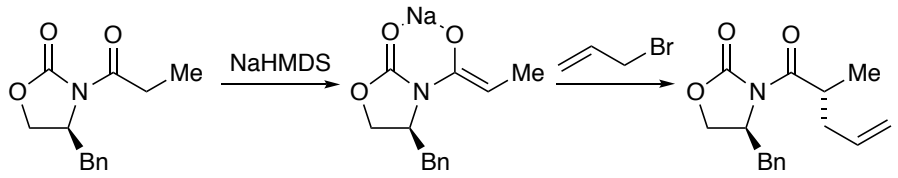
Structures and Reactivities of Sodiated Evans Enolates: Role of Solvation and Mixed Aggregation on the Stereochemistry and Mechanism of Alkylation

Abstract

Oxazolidinone-based sodiated enolates (Evans enolates) were generated using sodium diisopropylamide (NaDA) or sodium hexamethyldisilazide (NaHMDS) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), (*R,R*)-*trans*-*N,N,N′,N′*-tetramethylcyclohexanediamine [(*R,R*)-TMCDA], or (*S,S*)-TMCDA. ^{13}C NMR spectroscopic analysis in conjunction with the method of continuous variations (MCV) and density functional theory (DFT) computations revealed the enolates to be octahedral *bis*-diamine-chelated monomers. Rate and computational studies of an alkylation with allyl bromide implicate a *bis*-diamine-chelated-monomer-based transition structure. The sodiated Evans enolates form mixed dimers with NaHMDS, NaDA, or sodium 2,6-di-*tert*-butylphenolate, the reactivities of which are examined. Stereoselective quaternizations, aldol additions, and azaaldol additions of sodiated Evans enolates are described.

Introduction

Oxazolidinone-derived enolates—so-called Evans enolates—have been used in both academic and industrial laboratories in the development of asymmetric syntheses since they were first reported by Evans and co-workers in 1981.[1] Highly stereoselective functionalizations stemming from a wide variety of auxiliaries and counterions are legion.[2] Aldol additions typically rely on boron- or transition-metal-based enolates,[3] whereas alkylations require the more reactive sodium and lithium enolates.[1,4]



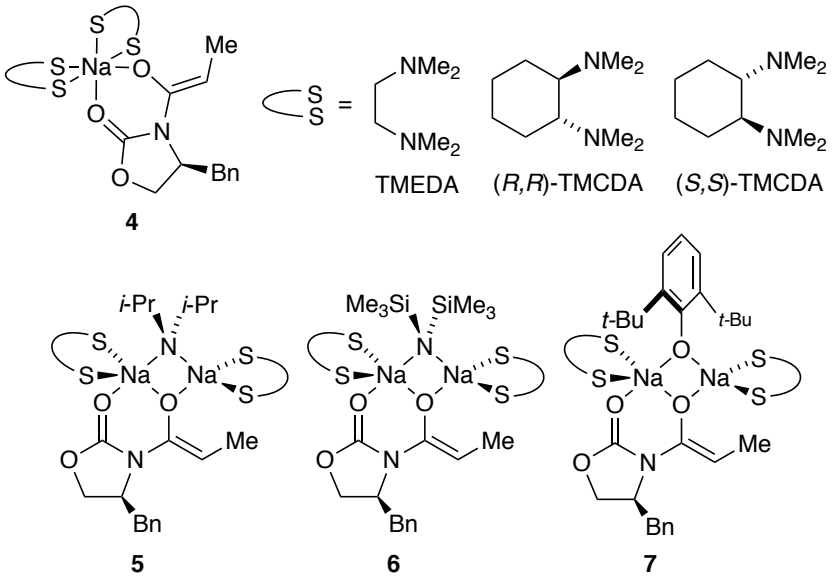
1 **2** **3** (2.1)

We previously characterized the structures of lithiated Evans enolates as tetramer–dimer mixtures in tetrahydrofuran (THF) solution,[5] underscored potential applications in simple aldol additions,[6,7] and demonstrated doubly diastereoselective aldol additions using lithium enolate–lithium amino alkoxide mixed tetramers.[8] We have also examined the structures and reactivities of key intermediates in di-*n*-butylboron triflate-based aldol additions.[9,10]

This paper examines the corresponding sodium enolates. Sodium enolate **2** in neat THF shows broad ^{1}H and ^{13}C resonances reminiscent of the poor structural control of simple sodium enolates in THF solution.[11] Although the use of THF is prevalent throughout organolithium chemistry,[12,13] could it be that the almost irresistible urge to use THF as the default medium may be suboptimal for organosodium compounds?

Structural, mechanistic, and stereochemical studies of sodiated Evans enolates generically depicted as **2** (eq 2.1) in toluene solutions with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and related *N,N,N′,N′*-tetramethylcyclohexanediamines [(*R,R*)- and (*S,S*)-*trans*-TMCDA)] reveal octahedral monomers of general structure **4** (Chart 2.1). Moreover, vicinal diamines promote mixed dimers **5**–**7**. Studies of the structure and mechanism of alkylation are shaping our thinking about the ligand-based control of structure and selectivity in organosodium chemistry, and the results underscore the potential merits of diamine/hydrocarbon mixtures.

Chart 2.1. Structures of sodiated Evans enolates solvated by diamines.

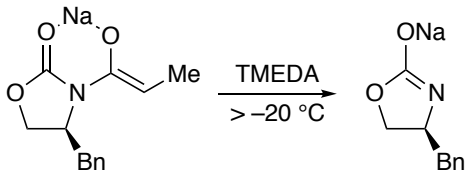


Results

General Methods. Sodium enolates were generated using either NaDA[14,15] or sodium hexamethyldisilazide (NaHMDS)[16,17] (recrystallized) dissolved in diamine/toluene solutions. Although the two bases afford similar results, NaHMDS is superior in this case owing to its ease of handling, commercial availability, and in some cases, superior role in subsequent functionalizations stemming from reversible deprotonation. Structures and reaction coordinates were examined with density functional theory (DFT) computations at the B3LYP/6–31G(d) level of theory with single-point calculations at the MP2 level of theory.[18] We refer to generic enolate **2** and the more specific monomer **4** interchangeably, depending on the context.

Enolization with either 0.10 M NaDA or 0.10 M NaHMDS in 1.0 M TMEDA/toluene is essentially instantaneous at –78 °C. The IR spectra show the loss of **1** at 1783 cm^{-1} and the appearance of an absorbance at 1743 cm^{-1}. During rate studies of alkylations, however, IR spectroscopy proved to have limited value owing to mediocre resolution and distortions caused by the deposition of NaBr. Also of note, sodium enolate **2** shows none of the aggregate-derived aging effects that can plague the highly aggregated lithium enolates.[5,6] However, **2** decomposes above –20 °C, affording sodium salt **8** observed with in situ IR spectroscopy (eq 2.2; 1666 cm^{-1}).[19] Deacylated

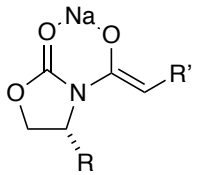
oxazolidinone along with debris that may derive from ketene were isolated on workup.[2b] The decomposition is approximately twofold slower in TMEDA/toluene than in THF solutions, which may be more consequential than one might suspect (*vide infra*).



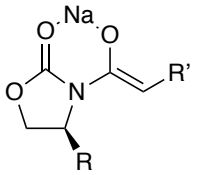
(2.2)

2 **8**

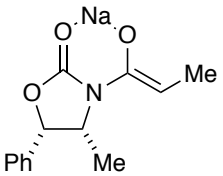
Structures of Enolate Monomers. ^{1}H and ^{13}C NMR spectroscopic studies of enolate **2** in the absence of excess NaDA or NaHMDS showed resonances corresponding to a single magnetically distinct subunit, as observed by monitoring the ^{13}C resonances of the oxazolidinone carbonyl carbon and the oxygen-bearing enolate carbon (δ157.3 and 152.7 ppm, respectively; Figure 2.1A). The diamine-solvated enolate was suggested to be monomeric when a synthetic racemate derived from (*S*)-**2** and (*R*)-**2** showed no resonances attributable to a heterochiral aggregate. Mixtures containing 1:1 pairs of enolate **2** with structurally analogous but spectroscopically distinct enolates **9a**–**d** as well as pairs containing **10** (six pairs in total) also showed no evidence of heteroaggregates (eq 2.3).[20] Emblematic ^{13}C NMR spectra of a binary mixture are shown in Figure 2.1B,C. Heteroaggregates were also not formed from enolate pairs solvated by either (*S,S*)-TMCDA or (*R,R*)-TMCDA.



(*R*)-**2**; R = Bn, R' = Me
(*R*)-**9a**; R = Bn, R' = Bn
(*R*)-**9b**; R = *i*-Pr, R' = Bn
(*R*)-**9c**; R = *i*-Pr, R' = Me



(*S*)-**2**; R = Bn, R' = Me
(*S*)-**9a**; R = Bn, R' = Bn
(*S*)-**9d**; R = Bn, R' = *i*-Pr



10

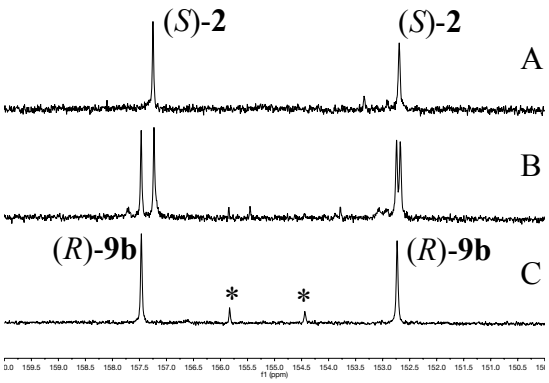
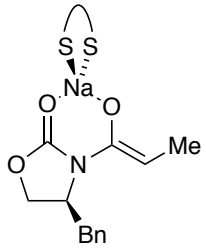


Figure 2.1. Partial ^{13}C NMR spectra of a mixture (*S*)-**2** and (*R*)-**9b** (with 0.20 M total enolate titer) in 1.0 M TMEDA in toluene recorded at –80 °C: (A) pure (*S*)-**2**; (B) equimolar (*S*)-**2** and (*R*)-**9b**; (C) pure (*R*)-**9b**. *Denotes the enolate–NaHMDS mixed aggregate **6**.

$$(\text{enolate A})_n + (\text{enolate B})_n \rightleftharpoons (\text{enolate A})_x(\text{enolate B})_y \quad (2.3)$$

not observed

At the outset, we presumed that the monomers were four-coordinate chelates of general structure **11**. However, binary mixtures of diamines afforded homo- and heterosolvates (eq 2.4) that could be resolved by ^{13}C NMR spectroscopy, as shown in Figure 2.2. The peak broadening in the samples containing mixed solvates is consistent with stereoisomerism delineated in the discussion. Despite the substandard spectral quality, we could use the method of continuous variations (MCV)[21] to confirm the structure as a doubly TMEDA-chelated monomer. Varying the diamine proportions in TMEDA/(*S,S*)-TMCDA mixtures and monitoring the homo- and heterosolvates versus *measured* mole fraction of TMEDA (χ_{TMEDA}) afforded a Job plot[22] with a unexpectedly good fit to the disolvate model (Figure 2.3).



11
(*not observed*)

$$\mathbf{2}(\text{TMEDA})_2 + \mathbf{2}(\text{TMCDA})_2 \rightleftharpoons \mathbf{2}(\text{TMEDA})(\text{TMCDA}) \qquad (2.4)$$

($\mathbf{2}L_2$) ($\mathbf{2}L'_2$) ($\mathbf{2}LL'$)

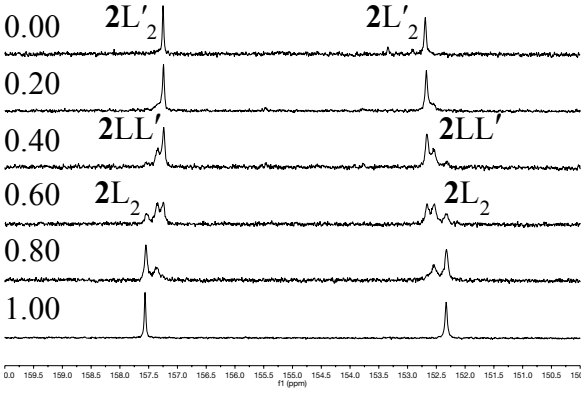


Figure 2.2. Partial ^{13}C NMR spectra of a mixture with 0.20 M enolate **2** and 1.0 M total TMEDA (L) and (*S*,*S*)-TMCDA (L′) concentration in toluene at –80 °C showing *bis*-TMEDA-solvated monomer ($\mathbf{2}L_2$), *bis*-TMCDA-solvated monomer ($\mathbf{2}L'_2$), and mixed solvated monomer ($\mathbf{2}LL'$; see eq 2.4). The *intended* mole fractions for TMEDA, X_B, are as labeled.

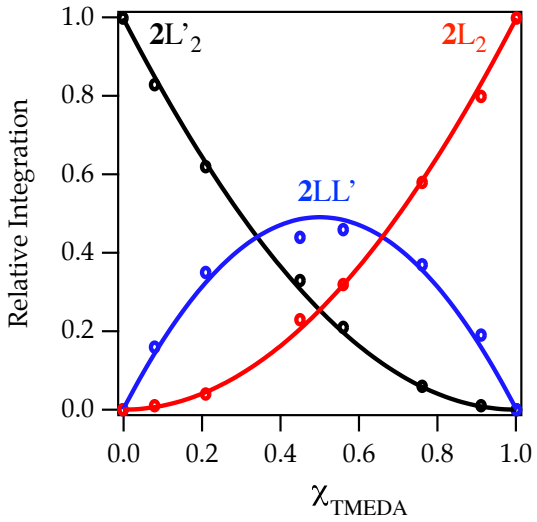


Figure 2.3. Job plot showing the relative integrations of *bis*-TMEDA-solvated monomer (**2**L_2), *bis*-TMCDA-solvated monomer (**2**L'_2), and mixed solvated monomer (**2**LL') versus the *measured* mole fraction of TMEDA for 0.20 M enolate (**2**) and TMEDA/(*S,S*)-TMCDA mixtures (1.0 M total diamine concentration) in toluene at −80 °C.

MCV can present a dangerous trap, exemplified by the Job plot in Figure 2.3, that is worthy of elaboration. Using measured mole fraction—the mole fraction determined by monitoring only ligand within the ensemble of interest—eliminates distortions arising from measuring errors, impurities, and side equilibria. It also precludes the influence of binding constant on the position of maxima.[21] By contrast, using the standard approach of plotting integration versus *intended* mole fraction—the mole fraction of the amines added within the total sample—provides the decidedly different result shown in Figure 2.4. It might be tempting to conclude from Figure 2.4 that TMEDA and (*S,S*)-TMCDA bind in a 2:1 stoichiometry. In this case, however, the skewing of the maximum to higher χ_{TMEDA} reflects the higher binding affinity of (*S,S*)-TMCDA relative to that of TMEDA.

One can (and we have[23]) extracted binding constants from such Job plots. (*S,S*)-TMCDA shows a –0.5 kcal/mol (exothermic) preference for substituting the first TMEDA and an attenuated –0.2 kcal/mol preference for substituting the second TMEDA. Computations predict –0.7 kcal/mol and –0.1 kcal/mol, respectively. Had the differential binding been more dramatic, the maximum would have been pushed even closer to the

right-hand *y*-axis. An analogous Job plot shows that sequential substitutions of TMEDA by (*R,R*)-TMCDA are nearly thermoneutral (+0.1 and –0.1 kcal/mol, respectively).

Summarizing an important point, using a simple binary system in which two species, A and B, bind to each other poses no lurking risk because the relative binding constants are *by definition* identical: the maximum in the curve reflects the relative stoichiometries. If two species—ligands in this case—compete for binding to a third entity (sodium), however, differential binding eliminates the relationship of the maximum and the stoichiometry of binding. This risk has inspired one group to declare the "death of the Job plot."[24] Although we think that declaration is a bit hyperbolic, such concerns should be heeded.

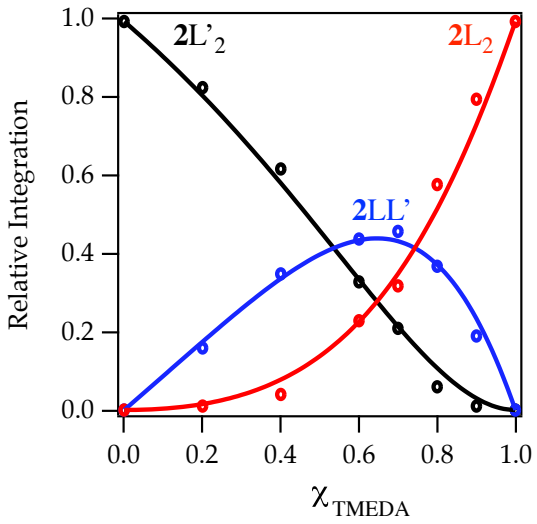


Figure 2.4. Job plot showing the relative integrations versus the *intended* mole fraction of TMEDA for a mixture of 0.20 M of enolate **2** and 1.0 M total diamine concentration in TMEDA/(*S,S*)-TMCDA mixtures in toluene at −80 °C. The shift in the maximum to $\chi_{TMEDA} > 0.50$ reflects the stronger binding of (*S,S*)-TMCDA.

The veracity of the assignment of enolate **2** as the *bis*-chelated octahedral monomer **4** is supported by DFT computations showing the exothermic serial solvation of unsolvated enolate monomer **2** (eq 2.5). The octahedral geometry is illustrated in Figure 2.5 using the lowest energy stereoisomer of **4**. A more elaborate description of the

stereochemistry of chelation is deferred to the discussion.

$$\mathbf{2} \underset{\text{(–23.3 kcal/mol)}}{\overset{\text{TMEDA}}{\rightleftharpoons}} \mathbf{2}(\text{TMEDA}) \underset{\text{(–17.2 kcal/mol)}}{\overset{\text{TMEDA}}{\rightleftharpoons}} \mathbf{2}(\text{TMEDA})_2 \quad (2.5)$$

(**11**) (**4**)

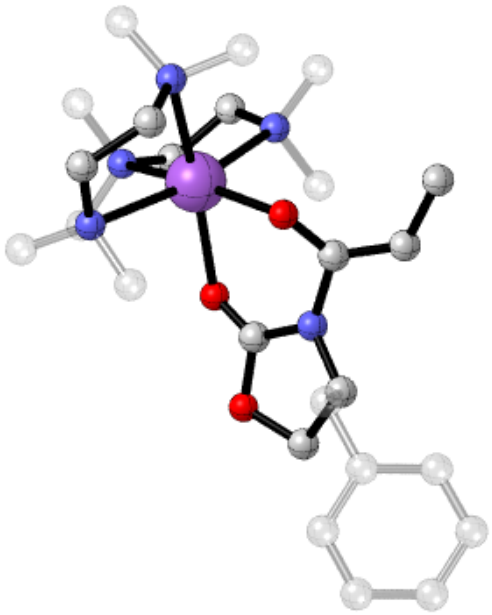


Figure 2.5. Computed structure of *bis*-chelated monomer **4** as its lowest energy delta stereoisomer.

Structures of Enolate–Amide Mixed Dimers. The enolization of **1** with excess NaDA or NaHMDS generates additional enolate ^{13}C resonances manifesting amide-concentration-dependent intensities and amide-dependent chemical shifts (Figure 2.6). These new species are assigned as mixed dimers **5** and **6**. The 1:1 stoichiometry in **6** is shown by the quantitative formation with 1.0 equiv NaHMDS (Figure 2.6) as reflected in the Job plot in Figure 2.7. By contrast, NaDA shows qualitatively similar behavior, albeit reflecting a soft equilibrium (Figures 2.8 and 2.9). Thus, *NaHMDS shows a greater penchant than NaDA for mixed aggregation*, which is the opposite of what is observed for LDA and LiHMDS.[25]

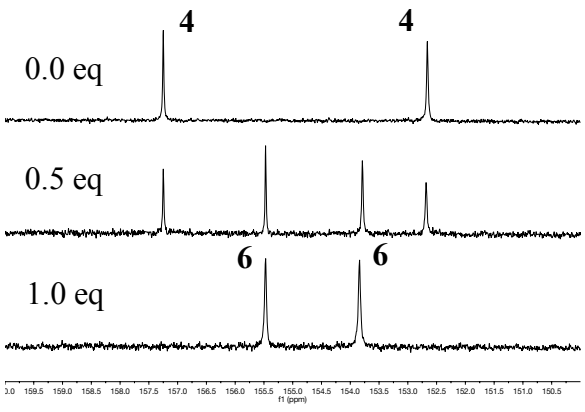


Figure 2.6. Partial ^{13}C NMR spectra of 0.20 M enolate **2** and 1.0 M TMEDA at various equivalents of excess NaHMDS (as indicated) in toluene at –80 °C showing monomer **4** and mixed dimer **6**.

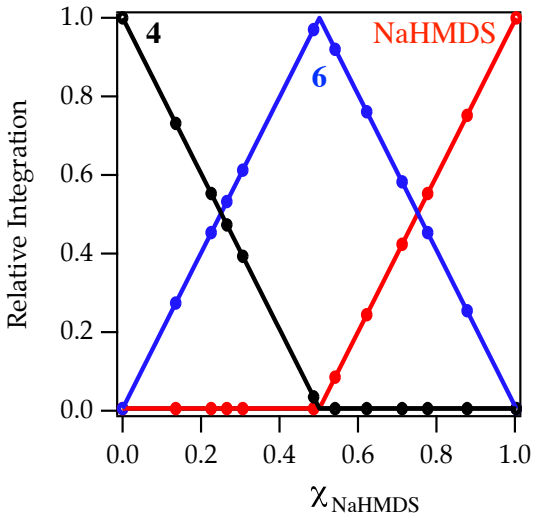


Figure 2.7. Job plot showing the relative integrations of NaHMDS (red), enolate monomer **4** (black), and mixed dimer **6** (blue) versus the *measured* mole fraction of NaHMDS with various proportions of NaHMDS and enolate (0.30 M total sodium titer) in 0.60 M TMEDA/toluene at −80 °C. The ratios were ascertained by following the resonances of monomer **4** (carbonyl carbon at δ157.3), mixed dimer **6** (carbonyl carbon at δ155.5 and Me_3Si carbon at δ7.52), and NaHMDS (Me_3Si carbon δ6.76 ppm).

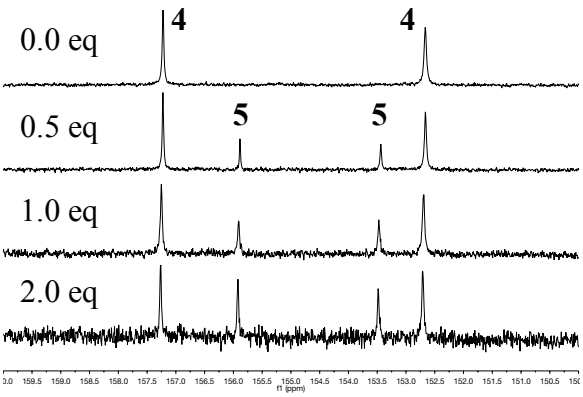


Figure 2.8. Partial ^{13}C NMR spectra of 0.20 M enolate **2** and 1.0 M TMEDA with various equivalents of excess NaDA (as indicated) in toluene at –80 °C. Monomer **4** and mixed dimer **5** are shown.

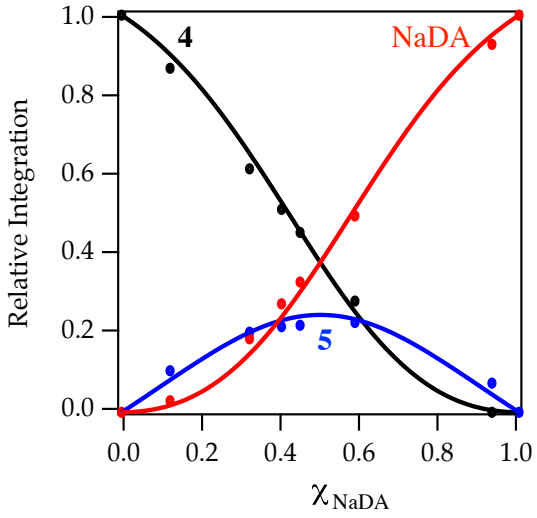
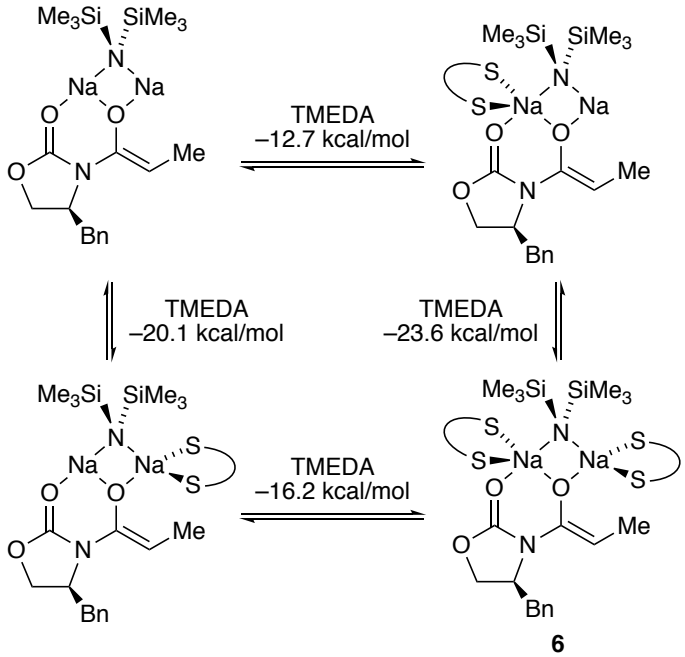


Figure 2.9. Job plot showing the relative integrations of NaDA (red), enolate monomer **4** (black), and mixed dimer **5** (blue) versus the *measured* mole fraction of NaDA with various proportions of NaDA and enolate (0.40 M total sodium titer) in 1.0 M TMEDA/toluene at −80 °C. The ratios were ascertained by following the resonances of monomer **4** (carbonyl carbon at δ157.3), mixed dimer **5** (carbonyl carbon at δ155.5 and NaDA methyne carbon at δ50.4), and NaDA (NaDA methyne carbon δ50.2 ppm).

We attempted to confirm the number of chelating ligands on mixed dimers **5** and **6** by integrating the ^{13}C resonances of free and bound TMEDA, but we were unable to obtain the necessary resolution. Nonetheless, decreasing the TMEDA concentration promotes NaDA mixed dimer **5**, consistent with a lower per-sodium solvation (eq 2.6).[15,26] DFT computations using the NaHMDS-derived mixed dimer **6** emblematically showed serial chelation by TMEDA to be exothermic for both the first and the second ligations (Scheme 2.1). The computed structure of the bis-chelate is illustrated in Figure 2.10. The planes defined by Na_2O_2 and the oxazolidinone chelated enolate are twisted by 50–60°.

$$\underset{\textbf{(4)}}{RONa(TMEDA)_2} + 1/2(i\text{-}Pr_2NNa)_2(TMEDA)_2 \rightleftharpoons \underset{\textbf{(5)}}{(RONa)(i\text{-}Pr_2NNa)(TMEDA)_2} + TMEDA \qquad (2.6)$$

Scheme 2.1. Serial solvation of NaHMDS to give mixed dimer **6**.



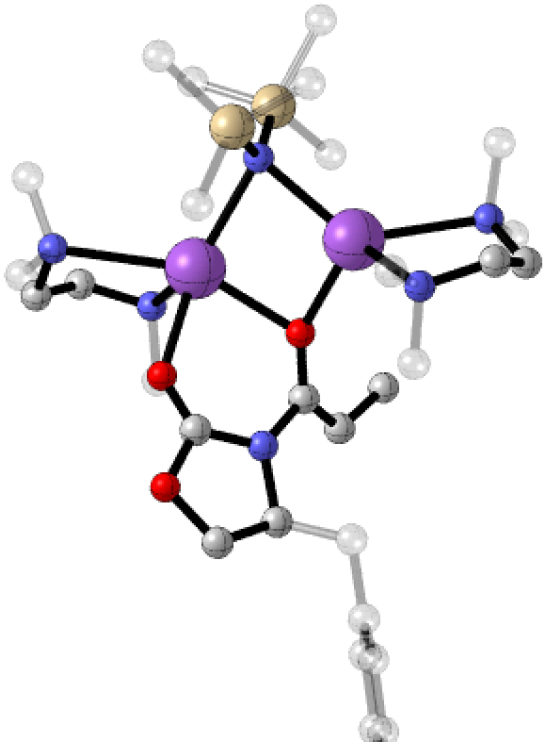


Figure 2.10. Computed structure of bis-TMEDA-chelated mixed dimer **6**.

Structures of Enolate–Phenolate Mixed Dimers. Hoping to exploit mixed dimers to control the selectivity of enolate functionalizations (*vide infra*), we found that insoluble sodium 2,6-di-*tert*-butylphenolate[27] suspended in TMEDA/toluene is solubilized by enolate **2** to form mixed dimer **7** quantitatively (Figure 2.11). The 1:1 enolate–phenolate stoichiometry was shown with ^{13}C NMR spectroscopy. Although ligand exchange was too fast for the direct measurement of the number of coordinated TMEDA ligands, DFT computations showed exothermic double chelation and support the structure in Figure 2.12. The phenolate moiety shows a significant cant away from the oxazolidinone for reasons that are not obvious. The approximate planes defined by the Na_2O_2 and oxazolidinone rings are skewed by >60°.

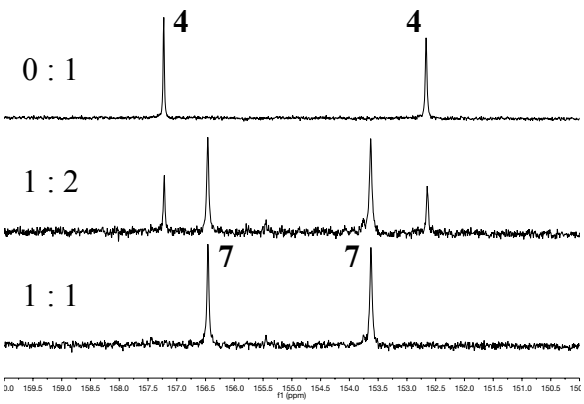


Figure 2.11. ^{13}C NMR spectra of mixtures containing enolate **2** and sodium 2,6-di-*tert*-butylphenolate (0.30 M total sodium titer) in 1.0 M TMEDA/toluene at –80 °C showing monomer **4** and mixed aggregate **7**. The concentrations of phenolate are 0.00, 0.10, and 0.15 (1.0 equiv), respectively.

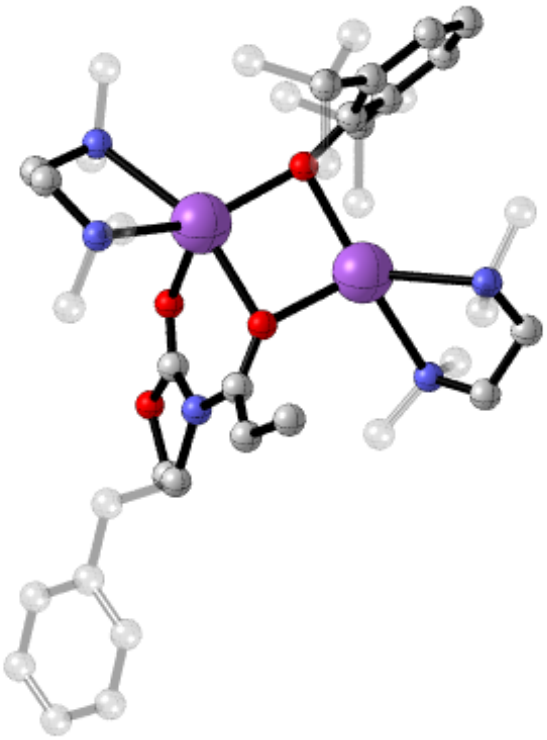


Figure 2.12. Computed structure of sodium 2,6-di-*tert*-butylphenolate-containing mixed dimer **7** solvated by TMEDA.

Kinetics of Alkylation.[28] Technical problems with using in situ IR spectroscopy to study the allylation of monomer **4** (generic enolate **2** in eq 2.1) prompted us to monitor the loss of allyl bromide with ^{1}H NMR spectroscopy. Pseudo-first-order conditions were established by maintaining standard concentrations of enolate **4** (0.050–0.50 M) and 2.0 equiv TMEDA per sodium (0.10–1.0 M) with low allyl bromide concentrations (0.010 M), all in toluene. The loss of allyl bromide follows a clean pseudo-first-order decay (Figure 2.13). Following an alkylation to full consumption of enolate shows no evidence of autoinhibition or autocatalysis. The other dependencies were determined using the method of initial rates.[29] Plotting initial rates versus enolate and TMEDA concentration revealed first and zeroth orders, respectively (Figures 2.14 and 2.15). The rate data are consistent with the idealized[30] rate law in eq 2.7 and the generic mechanism in eq 2.8. DFT computations suggest a massive 2000:1 preference at –20 °C (3.9 kcal/mol; eq 2.1) compared with the more modest 20:1 diastereoselectivity observed experimentally. The transition structures show no significant rotations about the N–C(ONa) bond compared with a 30° twist noted in the aldol additions by lithiated Evans enolates (Figure 2.16).[6] The TMEDA distal to the alkylating agent shows significant Na–N bond lengthening at the transition state that, according to IRC calculations, becomes pronounced as a Na–Br contact emerges.

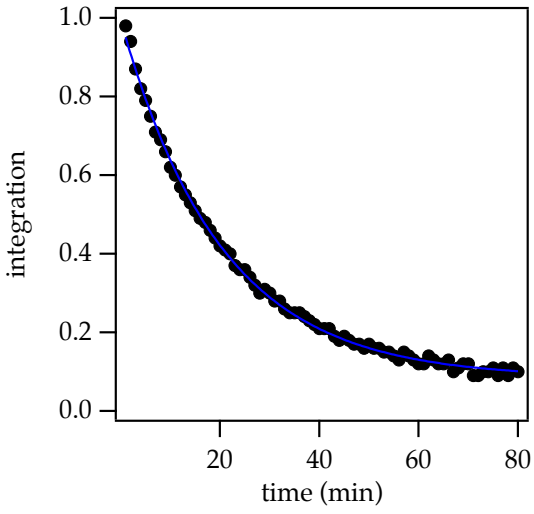


Figure 2.13. Plot following the loss of allyl bromide (0.010 M) by enolate monomer **4** (0.40 M) in 1.0 M TMEDA/toluene at –20 °C. The curve depicts a least squares fit to $y = ae^{-bx}$, such that $b = k_{obsd}$.[28]

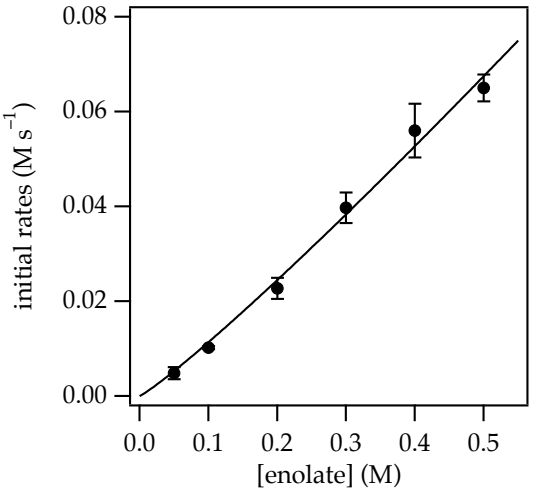


Figure 2.14. Plot of initial rates for the allylation of monomer **4** with allyl bromide (0.010 M) versus the enolate concentration at a fixed 2:1 TMEDA/enolate ratio in toluene. $y = ax^n$; $a = 0.15 \pm 0.01$; $n = 1.11 \pm 0.08$.

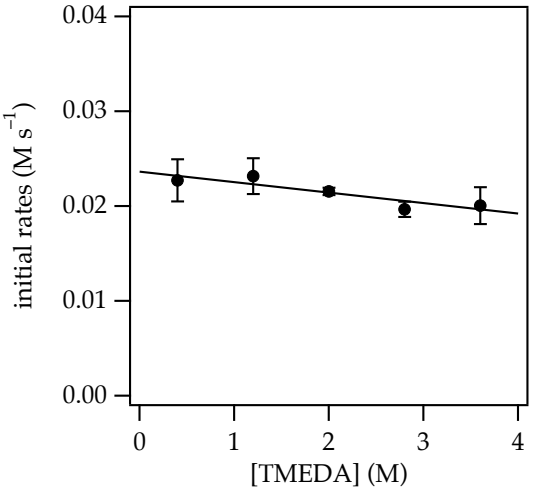


Figure 2.15. Plot of initial rates for the allylation of monomer **4** (0.20 M) with allyl bromide (0.010 M) versus *free* (unbound) TMEDA concentration in toluene. $y = ax + b$; $a = -0.0011 \pm 0.0003$; $b = 0.0236 \pm 0.0007$.

$$d[\mathrm{RBr}]/dt = k_{obsd}[\mathrm{RBr}]^1[\mathrm{RONa}]^1[\mathrm{TMEDA}]^0 \qquad (2.7)$$

$$(\mathrm{RONa})(\mathrm{TMEDA})_2 + \mathrm{RBr} \longrightarrow [(\mathrm{RONa})(\mathrm{TMEDA})_2(\mathrm{RBr})]^{\ddagger} \qquad (2.8)$$

4 **12**

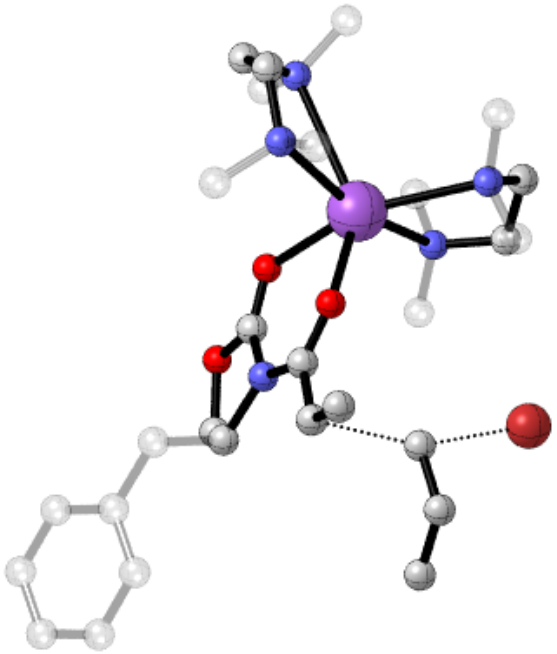
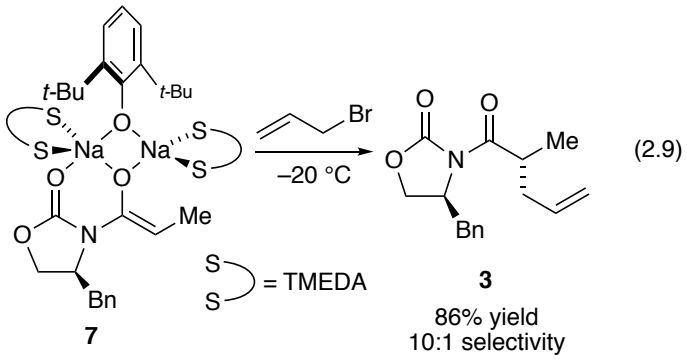


Figure 2.16. Computed lowest-energy anti transition structure **12** for the allylation of monomer **4**.

Solvent- and Salt-Dependent Selectivities. The choice of diamine has no discernible effects (±10%) on enolization rates, alkylation rates, or diastereoselectivities. Using THF, which affords a structurally complex enolate, alkylates twofold faster but is otherwise indistinguishable.

Allylations of mixed aggregates gave mixed results. Low yields and complex mixtures from **5** and **6** suggested that the sodium amides pose problems. The alkylation

of phenolate mixed aggregate **7**, by contrast, afforded a good yield but an eroded (10:1) diastereoselectivity (eq 2.9). The *change* in selectivity may be important (*vide infra*).



(2.9)

Quaternization. We examined a number of reactions of sodium enolates to ascertain how its structure influences selectivity. For example, Evans enolate-based quaternizations have been reported sporadically.[31] Presumed kinetic enolization of **13** using NaDA/TMEDA and subsequent alkylation afford free auxiliary (eq 2.2) resulting from enolate acylation[4a] and a more arcane decomposition of the oxazolidinone backbone.[32] The enolization of **13**[33] using NaHMDS and subsequent alkylation at –20 °C manifest highly solvent-dependent results (eq 2.10; Table 2.1). THF affords essentially no (<5%) quaternized product owing to facile deacylation (entry 1). By contrast, using NaHMDS in TMEDA/toluene affords a 54% yield of **14** as an 11:1 mixture of diastereomers (entry 2). Enolization and alkylation of diastereomer **15** afford the *same* 11:1 selectivity, which suggests that selectivity stems from an equilibrated *Z*/*E* enolate mixture (eq 2.11).

Curiously, accelerating the enolization merely twofold using NaHMDS/Et_3N/toluene[34] increases the yield to 70% with no measurable loss in stereoselectivity (11:1; entry 4). Under such poorly solvating conditions, precomplexation of the substrate was observable with IR.[35] Enolization using NaHMDS/Et_3N/toluene with *subsequent* addition of (*R*,*R*)-TMCDA gave identical results (entry 5). The isolated yields roughly correlate with the suppression of the deacylation. NaHMDS/(*R*,*R*)-TMCDA afforded improved selectivities (30:1) with a sacrificed yield (40%; entry 6), whereas NaHMDS/(*S*,*S*)-TMCDA gave 19:1 selectivity in 52% yield

(entry 7). Adding di-*tert*-butylphenolate (possibly forming an analog of mixed dimer **7**) gave the standard 11:1 selectivity in 44% yield (entry 8).

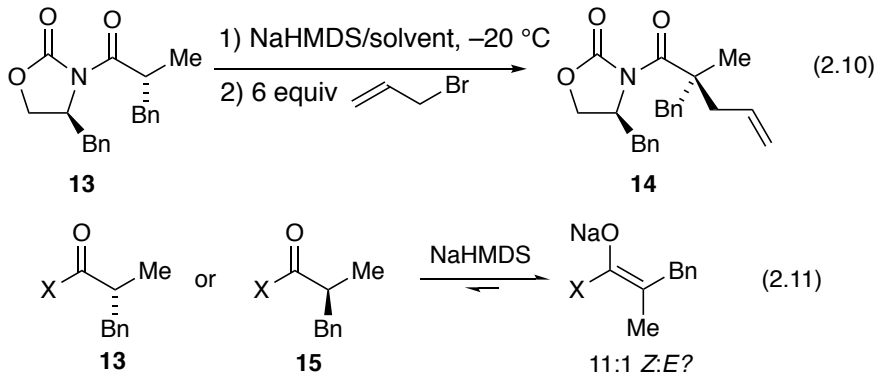


Table 2.1. Selectivities for quaternization of oxazolidinone **13** (eq 2.10).

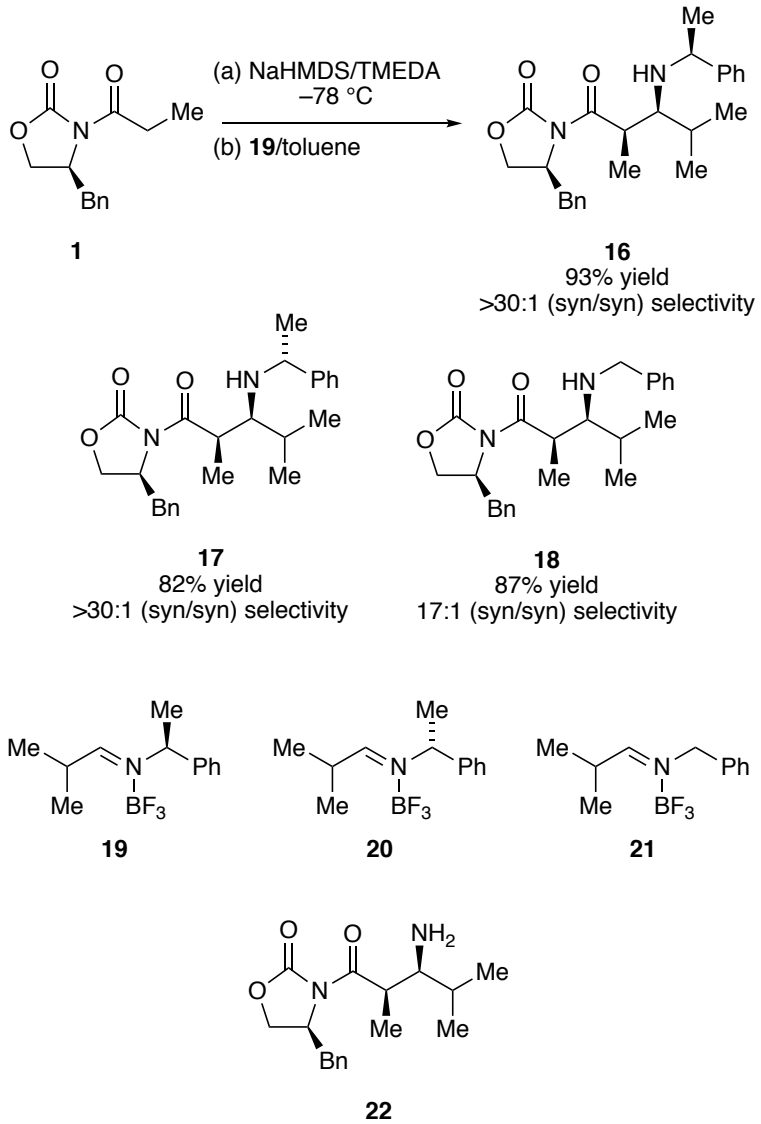
Entry	Solvent	Yield (%)	**14** (*S*/*R*)
1	THF	Decomp	
2	TMEDA	54	11:1
3	DME	40	11:1
4	Et_3N	70	11:1
5	Et_3N then (*R,R*)-TMCDA	71	11:1
6	(*R,R*)-TMCDA	40	30:1
7	(*S,S*)-TMCDA	52	19:1
8	**7**/TMEDA	44	11:1

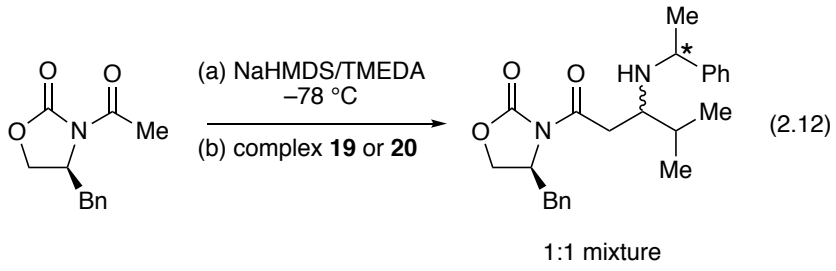
Azaaldol Additions. A brief examination of other electrophiles afforded nothing of interest with epoxides even with assistance from BF_3.[36] The azaaldol addition, however, proved productive. Simple imines are too unreactive to compete with enolate decomposition. Noting success using imines activated with strongly electron withdrawing substituents,[37,38,39,40] we turned to highly reactive BF_3–imine complexes[41] while adding the phenethyl moiety, hoping to amplify the stereocontrol (Scheme 2.2).[39]

The addition of BF_3–imine complex **19** dissolved in toluene to enolate **2** in TMEDA/toluene at –78 °C afforded adduct **16** in >30:1 selectivity and 93% yield. *Adding BF_3-Et_2O to an imine/enolate mixture was considerably less effective.* The

antipodal BF_3–imine complex **20** afforded **17** in an analogously high (>30:1) selectivity and 82% yield. Hydrogenolyses of **16** and **17** both afforded adduct **22**.[42] Thus, contrary to some 1,2-additions to phenethyl imines showing high stereochemical control,[40,43] the stereochemistry of the phenethylimine moiety had no effect whatsoever. Benzylimine–BF_3 complex **21** afforded adduct **18** in 17:1 stereoselectivity and 87% yield. The steric demands of the phenethyl moiety may have some consequence. We hoped that even acetate-based azaaldols would be selective, but no stereocontrol was observed (eq 2.12).

Scheme 2.2. 1,2-Additions of enolate **2** to imine–BF_3 complexes.

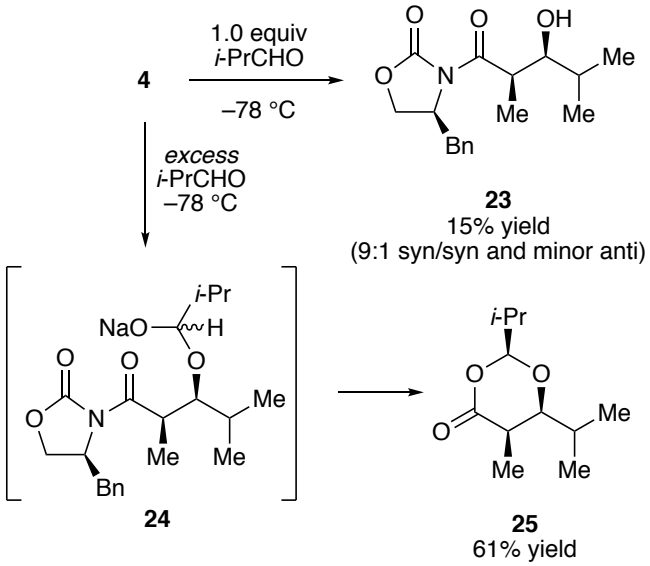




(2.12)

Aldol Additions. Aldol addition to 1.0 equiv *i*-PrCHO afforded a low yield of aldol **23** owing to the formation of acetal **25** with credible stereocontrol (Scheme 2.3). Aldol addition in the presence of excess *i*-PrCHO afforded acetal **25** contaminated with approximately 10% total of three minor diastereomers in a non-optimized 61% isolated yield. Acetal **25** presumably forms via 1,2-adduct **24**. Treating stereochemically pure syn aldol adduct **23** sequentially with 1.0 equiv of NaHMDS (to generate the alkoxide) and *i*-PrCHO afforded **25** in an unoptimized 59% yield with no loss of syn stereoselectivity. Acetal **25** from the aldol addition-cyclization sequence was shown to be an 7:1 mixture of enantiomers reflecting the original syn:syn selectivity.[44]

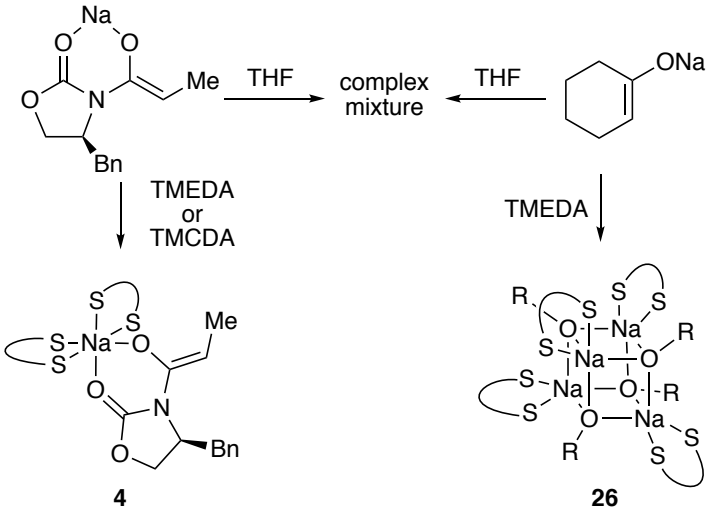
Scheme 2.3. Aldol addition and aldehyde-mediated deacylation.



Discussion

Structures of TMEDA-Solvated Enolates. Our fledgling studies of sodiated enolates have produced decidedly different results than studies of their lithium counterparts (Scheme 2.4).[12] For example, lithium cyclohexenolate is tetrameric in THF and a doubly chelated dimer in TMEDA/toluene.[45] By contrast, sodium cyclohexenolate is intractably complex in THF and forms chelated tetramer **26** in TMEDA/toluene.[11] Similar bifurcated behavior is observed with Evans enolates. Lithiated Evans enolates are predominantly unsolvated tetramers in either TMEDA or THF.[5] The sodium analogs are, once again, spectroscopically intractable in THF yet exclusively chelated monomers (**4**) in TMEDA/toluene.

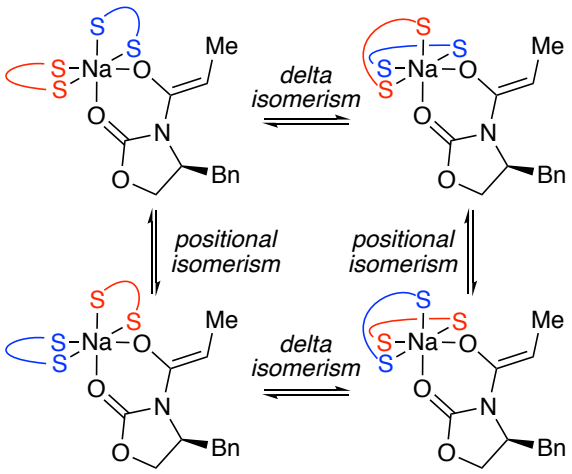
Scheme 2.4. Structures of sodium enolates in THF and TMEDA/toluene.



The *two* chelating diamines in **4** cause highly characteristic mixed solvates in binary mixtures of TMEDA, (*R,R*)-TMCDA, and (*S,S*)-TMCDA. The details were obscured by broadened resonances and limited resolution that attest to the stereochemical complexity presented by the octahedral environment of **4** (Scheme 2.5). If the chelated diamines in **4** (depicted using red and blue color coding) are both TMEDA, there are two delta isomers[46] suggested by DFT computations to have nearly equal energy (0.4 kcal/mol; see Figure 2.5). Each delta isomer contains two magnetically inequivalent TMEDA ligands manifesting eight magnetically inequivalent methyls—16 in total. In the

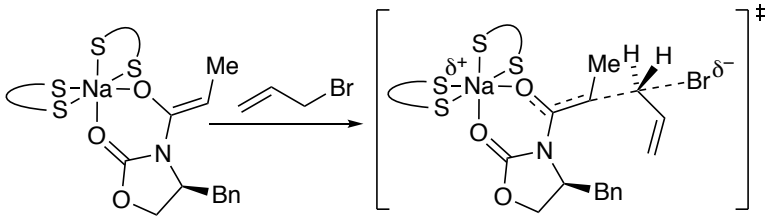
limit of slow conformational exchange of TMEDA, half-chair conformers that are well-documented for TMEDA–lithium chelates[47] would cause that number to spike. The stereochemical complexity doubles with mixtures of structurally distinct diamines (denoted as red and blue in Scheme 2.5) when delta isomerism and *positional* isomerism are superimposed. DFT computations predict the four isomers in Scheme 2.5 to be within <1.0 kcal/mol for the (*S,S*)-TMCDA/TMEDA mixed solvate, for example. Thus, we were *never* going to resolve all the magnetically inequivalent resonances and consider it fortunate that we could detect and measure the total populations of the mixed and homosolvates by focusing on the enolate sp^2 carbons.

Scheme 2.5. Positional and delta isomers of octahedral monomeric enolates.



Mechanism and Stereochemistry of Alkylation. The mechanism of alkylation of monomer **4** is simple, occurring via a doubly chelated monomer (Figure 2.16) without any invasive structural changes. DFT computations markedly overestimate the observed 20:1 selectivity but are qualitatively consistent (eq 2.13). The simplicity of an observable monomer reacting as monomer contrasts with the reaction of lithium Evans enolates in THF solution, in which a kinetically generated mixture of isomeric dimers readily ages to predominantly tetramer, and with the reaction of enolate **2** in THF, which seems to exist as an ill-defined but obviously quite complex mixture of species. Owing to pre-equilibria, explicit correlations of observable structure with reactivity and selectivity are questionable. Nonetheless, years of experience have shown that high stereocontrol is

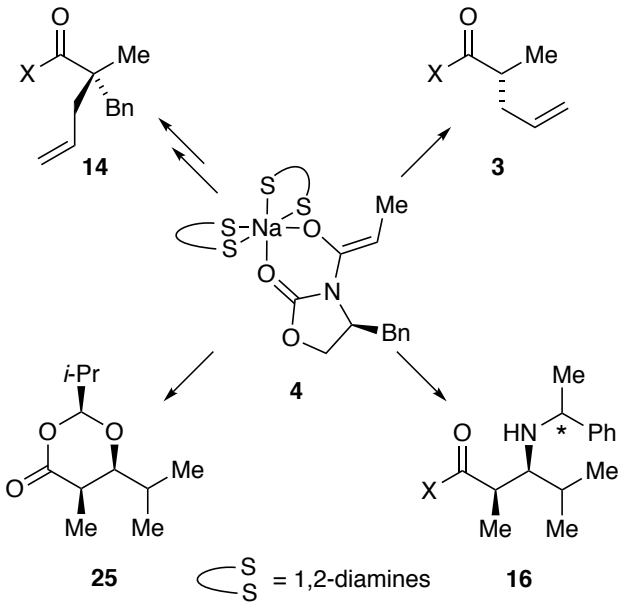
often accompanied by good structural control. For the allylation in eq 1, we observed no advantages or disadvantages offered by TMEDA/toluene compared with THF, but that is not universally the case (*vide infra*).



4 **12** (2.13)

Enolate Quaternization. There are relatively few quaternizations of Evans enolates, and they tend to be specialized cases such as those bearing sterically undemanding a-fluoro or a-alkoxy moieties.[31,48] In our hands, the quaternization (Scheme 2.6 and eq 2.10) completely fails in THF solution owing to competitive deacylation. By contrast, TMEDA-solvated enolate—presumably a bis-chelated monomer analogous to **4**—gave 54% yield and 11:1 diastereoselectivity. The stereochemistry appeared to be dictated by a fully equilibrated *Z*/*E* enolate mixture. There are potentially superior protocols,[31] but quaternizations of TMEDA-solvated Evans enolates may find a niche and certainly underscore a uniqueness of monomeric enolate **4**.

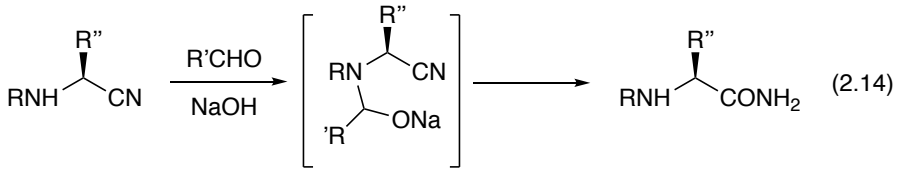
Scheme 2.6. Reactions of diamine-solvated monomeric enolate **4**.



Other Electrophiles. A casual survey of electrophiles showed that TMEDA-solvated monomer **4** might find broader applications (Scheme 2.6). The most notable results come from additions of **4** to pre-formed imine-BF_3 complexes. 1,2-Additions of Evans enolates to activated imines are rare.[38] Although the addition formed adduct **16** in good yield with essentially total stereoselectivity (>30:1), the choice of phenethylimine antipode had no influence on the selectivity whatsoever; the oxazolidinone auxiliary was the dominant control element. Equally surprising on the other end of the scale, an acetate-based addition was totally unselective irrespective of the phenethylimine antipode.

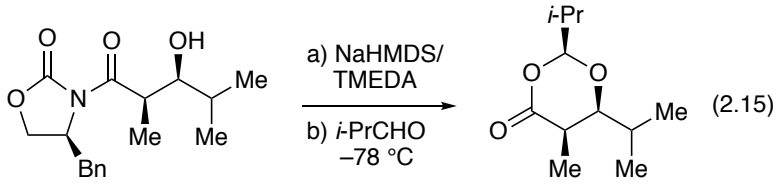
We suspect that relatively few attempts have been made to exploit sodiated Evans enolates for aldol additions; we found one report.[49] This is to be expected given the limited attention received by their lithium counterparts.[7] Indeed, we observed low yields of addition to *i*-PrCHO, albeit with a credible stereoselectivity (Scheme 2.3). The major byproduct was acetal **25**, presumably formed via 1,2-adduct **24**. Using excess *i*-PrCHO affords acetal **25** in 61% yield (Scheme 2.3). We suspect that the diastereoselective cyclization required to control the stereochemistry at the acetal-based stereogenic center arises from reversible adduct formation and selective closure. Adduct **24** is reminiscent of the compounds exploited by Beauchemin and co-workers using aldehydes as organocatalysts (eq 2.14),[50] as well as the key intermediates in a tandem aldol addition

and Tishchenko reaction.[51] We have previously suggested that transiently and reversibly formed 1,2-adducts may be prevalent but undetected.[6]



(2.14)

The formation of **25** poses a number of synthetically notable possibilities. Precluding the retroaldol may be the source of the markedly increased yield relative to that of the simple aldol addition. A potentially four-pot sequence—aldol addition, alcohol protection, deacylation, and esterification—is telescoped to one in >90% yield per step. The premature removal of the auxiliary, however, causes the stereochemical refinement of adducts analogous to **23** to become a problem of refining optical purity. In the spirit of Beauchemin's results, stereochemically pure syn aldol adduct **23** can be transformed to **25** in a single step with an unoptimized 59% yield and no loss of diastereoselectivity (eq 2.15). This one-step replacement of what would otherwise be a three-step protocol may have some synthetic utility in polyketide synthesis.



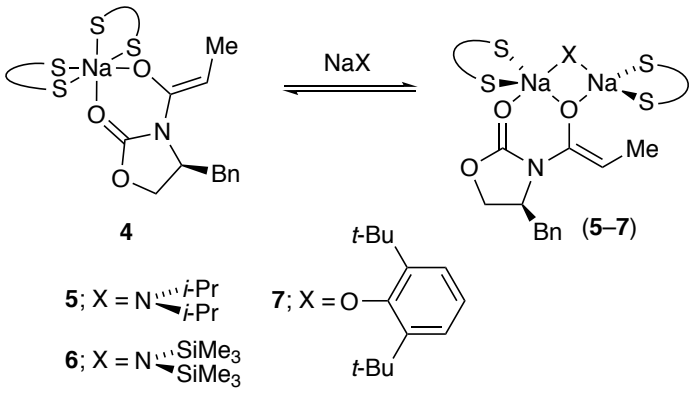
(2.15)

23 **25**
59% yield

Mixed Aggregate Structure and Reactivity. Admittedly limited studies to date have shown little evidence of mixed aggregation in NaDA/NaX mixtures,[52,53] which is quite unlike the often-observed LDA–LiX mixed aggregates.[25] We were surprised, therefore, to observe sodium enolate–sodium amide mixed dimers **5** and **6** (Scheme 2.7). Moreover, NaHMDS forms mixed dimer **6** quantitatively, whereas the analogous NaDA–sodium enolate mixed dimer **5** is formed in a much softer (non-quantitative) equilibrium

given that the reverse is true for LiHMDS and LDA.[25] Even insoluble sodium di-*tert*-butylphenolate is drawn into solution to form mixed dimer **7** quantitatively.

Scheme 2.7. Mixed aggregation with Evans enolates.



Mixed aggregates **5**–**7** could impose stereochemical control over the alkylations *provided that the mixed aggregates react without dissociation to monomer **4**.*[54,55] Although alkylations of **5** and **6** gave poor results presumably owing to the nefarious reactivities of the sodium amide fragments, the phenolate-derived mixed dimer **7** showed promise: it reacted cleanly *and* altered the product distribution, albeit in the wrong direction (eq 2.9). Here is why we still find the experiment interesting. *If* mixed dimer **7** reacts directly without invasive structural changes, there is a stereocontrol element that is unavailable to monomer **4** (Figure 2.17). The monomer has a sodium and affiliated ligands in an s-trans orientation relative to the enolate carbon, placing potential stereochemically controlling ligands remote from the nucleophilic enolate carbon. By contrast, the dimer has an s-cis orientation. Despite early failures to improve the selectivity, we sense that persistence in the choice of salt (NaX) and diamine could lead to success.

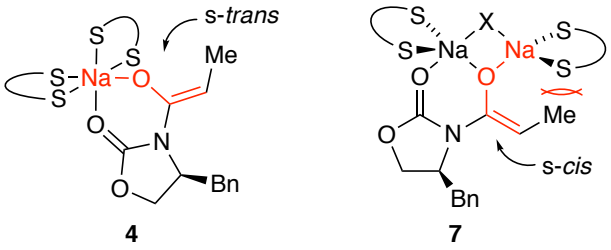


Figure 2.17. Illustration of *s-cis* and *s-trans* alignments.

Conclusion

Sodiated Evans enolates are often used for stereoselective alkylations; however, they are *not* just "lithium enolates on steroids." TMEDA-solvated monomer **4** has good structural control compared with the analogous enolate in THF solution and offers comparable alkylation selectivities and yields, allows for quaternizations, and exhibits potentially useful reactivities toward imines and aldehydes.

The contrasting behavior of THF and TMEDA raises an important issue. The development of organometallic chemistry is a story of ligand development and optimization. Whether we are speaking of transition-metal-catalyzed couplings or organolithium-based metalations, the coordination sphere is paramount. The temptation to use THF for sodium chemistry because it works so well for lithium may be misguided. Organolithium reagents dominate organoalkali metal chemistry despite lower reactivities because of their higher selectivities. We are not convinced that this will necessarily be the case going forward. Achieving high selectivities in organosodium chemistry may stem from the development of its ligands for the larger sodium ion.

Experimental

Reagents and Solvents. THF, TMEDA, TMCDA, and toluene were distilled from solutions containing sodium benzophenone ketyl. NaDA[14] and NaHMDS were prepared and purified as described previously.[16] Oxazolidinones are commercially available or prepared according to literature procedures.[56] Air- and moisture-sensitive materials were manipulated under argon with standard glove box, vacuum line, and syringe techniques.

IR spectroscopic analyses. IR spectra were recorded with an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired in 16 scans at a gain of 1 and a resolution of 4 cm^{-1}. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was capped with a septum for injections and a nitrogen line. After evacuation under full vacuum, heating, and flushing with nitrogen, the flask was charged with NaHMDS (101 mg, 0.55 mmol) in 1.0 M TMEDA/toluene, and cooled to –78 °C. After recording a background spectrum, oxazolidinone **1** (116.5 mg, 0.50 mmol) in toluene was added. The absorbance of **1** at 1783 cm^{-1} was immediately replaced with an absorbance of enolate **2** at 1743 cm^{-1}. To this solution was added neat allyl bromide (363 mg, 3.0 mmol), causing the enolate absorbance to be replaced by the absorbance of oxazolidinone **3** (1783 cm^{-1}). IR spectra were recorded every 15 s with monitoring of the absorbance at 1783 cm^{-1} over the course of the reaction.

NMR Spectroscopy. Individual stock solutions of substrates and NaHMDS were prepared at room temperature. An NMR tube under vacuum was flame-dried on a Schlenk line, allowed to cool to room temperature, backfilled with argon, and placed in a –78 °C dry ice/acetone bath. Appropriate amounts of oxazolidinone and NaHMDS (1.1 equiv) were added sequentially via syringe. The tube was sealed under partial vacuum, vortexed 3 times on a vortex mixer for 5 s with cooling between each vortexing. Samples could be stored overnight in a –86 °C freezer. Standard ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer at 500 and 125.79 MHz, respectively. The ^{1}H and ^{13}C resonances are referenced to $CDCl_3$ (7.26 and 77.16 ppm, respectively) and toluene-d_8 ($C_6D_5CD_3$ at 20.4 ppm).

NMR Reaction Kinetics. An NMR tube was charged with reagents as described above. The sample was vortexed 3 times on a vortex mixer for 5 s with cooling between each vortexing. To this solution, allyl bromide was added. The reaction was followed by ^{1}H NMR spectroscopy at –20 °C recording spectra at 1.0 min intervals.

Preparation of 3. To a solution of NaHMDS (0.60 mmol, 110 mg) and TMEDA (1.2 mmol, 180 μL) in 4.5 mL toluene under argon at –78 °C was added **1** (0.50 mmol, 116.5 mg) in 0.50 mL toluene. After stirring for 30 minutes, allyl bromide (3.0 mmol,

260 μL) was injected, and the vessel was warmed to 0 °C. The reaction was quenched by 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 20% ethyl acetate in hexanes provided 132 mg (97% yield) shown by ^1H NMR spectroscopy to be a 20:1 diastereomeric mixture of **3** and its isomer analogous to that reported previously.[33]

Preparation of 13. To a solution of NaHMDS (3.3 mmol, 605 mg) and TMEDA (6.6 mmol, 988 μL) in 5.0 mL toluene under argon at –78 °C was added **1** (3.0 mmol, 699 mg) in 1.0 mL of toluene. The reaction was stirred for 30 minutes, charged with benzyl bromide (20 mmol, 2.4 mL), warmed to 0 °C, and stirred for 0.5 h. The reaction was quenched with 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 20% ethyl acetate in hexanes afforded 825 mg of **13** (85% combined yield) displaying spectroscopic properties described previously.[33]

Preparation of 14. To a solution of NaHMDS (0.10 mmol, 18.3 mg) and TMEDA (0.20 mmol, 30 μL) in toluene (2.0 mL) under argon was added **13** (0.070 mmol, 22.6 mg) in 0.10 mL of toluene. Reaction was stirred under argon for 1 hour at –20 °C. Allyl bromide (0.40 mmol, 35 μL) was injected and the mixture was warmed to 0 °C over 2 hr. The reaction was quenched with 3.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 15% ethyl acetate in hexanes afforded 13.7 mg of product (54% combined yield) shown to be an 11:1 mixture of **14** and its minor diastereomer. ^1H NMR (599 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 7.23 – 7.19 (m, 5H), 5.77 (dddd, J = 16.9, 10.1, 8.0, 6.7 Hz, 1H), 5.11 (dq, J = 17.0, 1.6 Hz, 1H), 5.06 (ddt, J = 10.0, 2.0, 1.0 Hz, 1H), 4.61 (ddt, J = 10.7, 6.7, 3.3 Hz, 1H), 4.15 – 4.10 (m, 2H), 3.61 (d, J = 13.6 Hz, 1H), 3.18 (dd, J = 13.2, 3.3 Hz, 1H), 3.12 – 3.04 (m, 2H), 2.61 (dd, J = 13.2, 10.6 Hz, 1H), 2.29 (ddt, J = 14.3, 6.7, 1.4 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.07, 152.77, 137.72, 135.94, 134.39, 130.58, 129.54, 129.06, 128.20, 127.38, 126.74, 118.27, 66.43, 58.32, 50.54, 42.01, 40.73, 38.01, 23.38. m/z calculated for $(M+H)^+$ 364.19072, found 364.19097.

Confirming the structure of 14. To a solution of **14** (0.050 mmol, 18 mg) in THF (0.45 mL) and water (0.15 mL) at 0 °C was added H_2O_2 (30%, 40 mL) dropwise

and LiOH (2.4 mg) in water (0.10 mL). The reaction was warmed to 20 °C for 2 hr, cooled to 0 °C, and treated with Na_2SO_3 (56.8 mg) in water (0.3 mL) with stirring at 20 °C for 12 hr. The reaction was concentrated in vacuo and its pH was adjusted to 13 using NaOH at 0 °C. The aqueous solution was extracted three times with CH_2Cl_2 and pH brought to 1 using concentrated HCl at 0 °C. The mixture was extracted three times with EtOAc, dried over $MgSO_4$, and concentrated in vacuo to afford 7 mg of product (69% combined yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 3H), 7.20 – 7.14 (m, 2H), 5.82 (ddt, *J* = 18.5, 9.2, 7.4 Hz, 1H), 5.17 – 5.09 (m, 2H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.78 (d, *J* = 13.4 Hz, 1H), 2.53 (ddt, *J* = 13.8, 6.9, 1.3 Hz, 1H), 2.21 (ddt, *J* = 13.7, 7.7, 1.2 Hz, 1H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.05, 137.33, 133.75, 130.35, 128.23, 126.77, 118.76, 47.48, 44.89, 43.33, 20.72. m/z calculated for $(M+H)^+$ 205.12231, found 205.12198. $[\alpha]^{22}$ = +12, c 0.35, DCM. An authentic sample was prepared using the procedure of Myers and coworkers.[57] $[\alpha]^{22}$ = +24, c 0.5, CH_2Cl_2.

Preparation of imine adduct 16. To a solution of NaHMDS (1.0 mmol, 183 mg) and TMEDA (2.0 mmol, 300 μL) in toluene (4.5 mL) was added **1** (1.0 mmol, 233 mg) followed by stirring under argon for 30 min at –78 °C. A solution of imine-BF_3 complex **19** (1.0 mmol) in toluene (0.20 mL) was injected. After stirring for 30 m, the reaction was quenched by 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude product was analyzed with ^{1}H NMR showing **16** in >30:1 selectivity. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N afforded **16** (380 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 7.6, 2.8 Hz, 4H), 7.31 – 7.25 (m, 3H), 7.25 – 7.19 (m, 3H), 4.70 (ddt, *J* = 10.9, 7.2, 3.4 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.15 – 4.11 (m, 1H), 3.95 (p, *J* = 6.8 Hz, 1H), 3.86 (q, *J* = 6.5 Hz, 1H), 3.40 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.88 (dd, *J* = 6.2, 4.8 Hz, 1H), 2.60 (dd, *J* = 13.1, 10.4 Hz, 1H), 1.67 (pd, *J* = 6.9, 4.9 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.35, 153.32, 146.49, 135.64, 129.48, 129.13, 128.37, 127.46, 127.27, 127.02, 66.17, 61.44, 57.74, 55.71, 41.64, 38.38, 32.49, 24.25, 20.74, 17.86, 13.82. m/z calculated for $(M+H)^+$ 409.24857, found 409.24889.

Preparation of imine adduct 17. Adduct **17** was prepared as described for adduct **16** using imine-BF_3 complex **20**. ^{1}H NMR spectroscopy of the crude shows **17** in

>30:1 selectivity. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N) afforded **17** in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.24 (m, 3H), 7.22 – 7.16 (m, 3H), 4.63 (ddt, *J* = 10.8, 7.3, 3.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.09 (dd, *J* = 9.1, 3.4 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.25 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.87 (dd, *J* = 6.7, 4.2 Hz, 1H), 2.52 (dd, *J* = 13.2, 10.3 Hz, 1H), 1.80 (pd, *J* = 6.9, 4.2 Hz, 1H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.23, 153.22, 146.33, 135.63, 129.48, 129.09, 128.42, 127.43, 127.16, 127.00, 66.04, 60.80, 56.84, 55.53, 40.84, 38.16, 31.84, 24.32, 20.67, 18.09, 14.15. m/z calculated for $(M+H)^+$ 409.24857, found 409.24796.

Preparation of imine adduct 18. Adduct **18** was prepared as described for adduct **16** using imine-BF_3 complex **21** in 87% yield. ^{1}H NMR spectroscopy of the crude shows **18** and its minor diastereomer in 17:1 selectivity. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N afforded **18** (34.3 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 7.24 – 7.21 (m, 3H), 4.73 (ddt, *J* = 11.0, 7.3, 3.5 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.14 (dd, *J* = 9.1, 3.6 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.86 (d, *J* = 12.5 Hz, 1H), 3.81 (d, *J* = 12.5 Hz, 1H), 3.40 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.90 (t, *J* = 6.0 Hz, 1H), 2.60 (dd, *J* = 13.1, 10.4 Hz, 1H), 1.81 (pd, *J* = 13.3, 6.7 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.99, 153.30, 141.05, 135.60, 129.43, 129.09, 128.46, 128.28, 127.42, 127.06, 66.20, 64.67, 55.57, 55.30, 41.14, 38.33, 32.33, 20.42, 18.83, 12.57. m/z calculated for $(M+H)^+$ 395.23292, found 395.23215.

Hydrogenolysis. To a solution of **17** (0.08 mmol, 33.3 mg) in methanol (2 mL) was added palladium on carbon (0.008 mmol, 8.5 mg). Reaction was stirred under 1.0 atm of H_2 for 24 hr at room temperature. After filtering through Celite and concentrating in vacuo, flash chromatography with 3% triethylamine in ethyl acetate afforded **22** (14.5 mg, 60% yield). Peak broadening presumably owing to hydrogen bonding was mitigated by warming to 60 °C. ^{1}H NMR (599 MHz, $CDCl_3$, 60 °C) δ 7.26 – 7.25 (m, 1H), 7.25 – 7.20 (m, 3H), 7.20 – 7.16 (m, 1H), 5.17 – 5.05 (m, 2H), 4.02 – 3.95 (m, 1H), 3.83 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.24 (dd, *J* = 13.7, 9.7 Hz, 1H), 3.12 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.66 (p, *J* = 7.0 Hz, 1H), 1.64 (pd, *J* = 14.0, 6.9 Hz, 1H), 0.97 – 0.87 (m, 3H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.32, 155.43,

138.18, 129.51, 128.49, 126.62, 63.85, 60.55, 55.92, 34.67, 27.90, 18.77, 18.18, 14.35, 9.89. m/z calculated for $(M+H)^+$ 305.18597, found 305.18521.

Aldol Addition. To a solution of NaHMDS (0.3 mmol, 54.9 mg) and TMEDA (0.9 mmol, 144 μL) in toluene (3 mL) was added **1** (0.3 mmol, 69.9 mg) in 0.10 mL of toluene. After stirring under argon for 30 min at –78 °C isobutyraldehyde (0.9 mmol, 82 μL) was injected and the mixture was stirred for 1 hr at –78 °C. After quenching with 1.0 mL saturated NH_4Cl and extracted three times with EtOAc, the organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 10% ethyl acetate in hexanes afforded 36.4 mg of **25** (61% combined yield). ^1H NMR showed a 17:1:0.7:0.4 mixture of **25** and three minor stereoisomers. ^1H NMR (599 MHz, $CDCl_3$) δ 5.06 (d, J = 4.2 Hz, 1H), 3.39 (dd, J = 9.0, 3.7 Hz, 1H), 2.73 (qd, J = 7.2, 3.7 Hz, 1H), 1.98 (hd, J = 6.9, 4.2 Hz, 1H), 1.84 (dh, J = 9.0, 6.6 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H), 1.01 – 0.97 (m, 9H), 0.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.94, 106.45, 82.07, 38.20, 32.71, 28.45, 18.67, 17.60, 16.17, 15.83, 11.74. m/z calculated for $(M+H)^+$ 201.14852, found 201.14824.

Chapter 2 Appendix

Chapter 2 Appendix Table of Contents

1. Aging effect

1. Aggregation study

3. Solvation study

4. 2D NMR

5. Alkylation kinetics

8. Aza-aldol Reaction

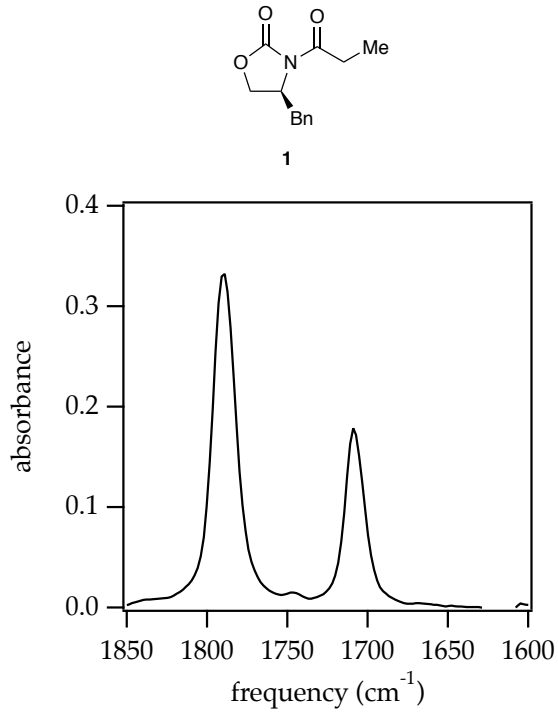


Figure A.2.1. IR spectrum of 0.10 M **1** in toluene recorded at –78 °C.

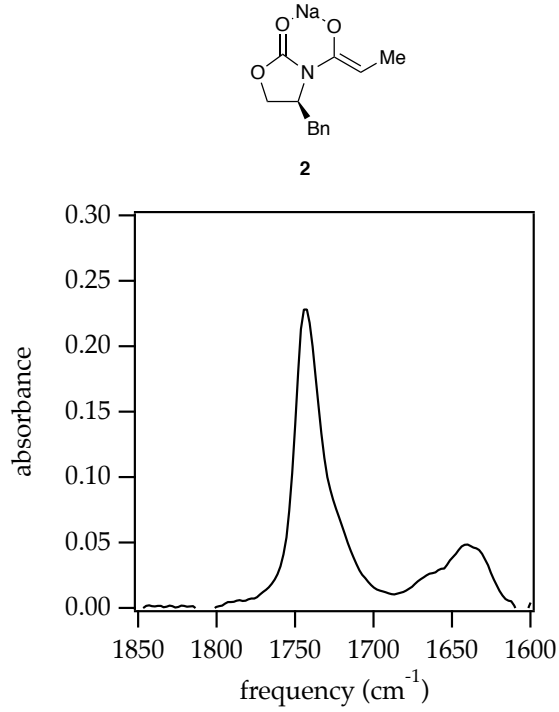


Figure A.2.2. IR spectrum of 0.10 M **2** in 1.0 M TMEDA/toluene recorded at –78 °C.

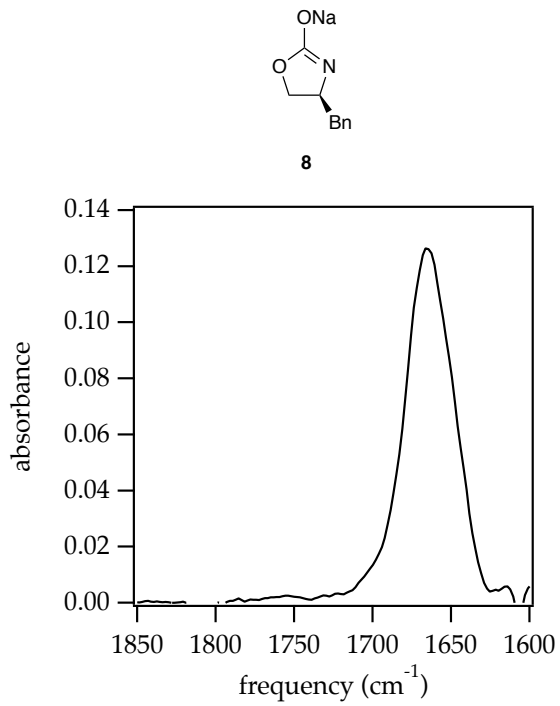
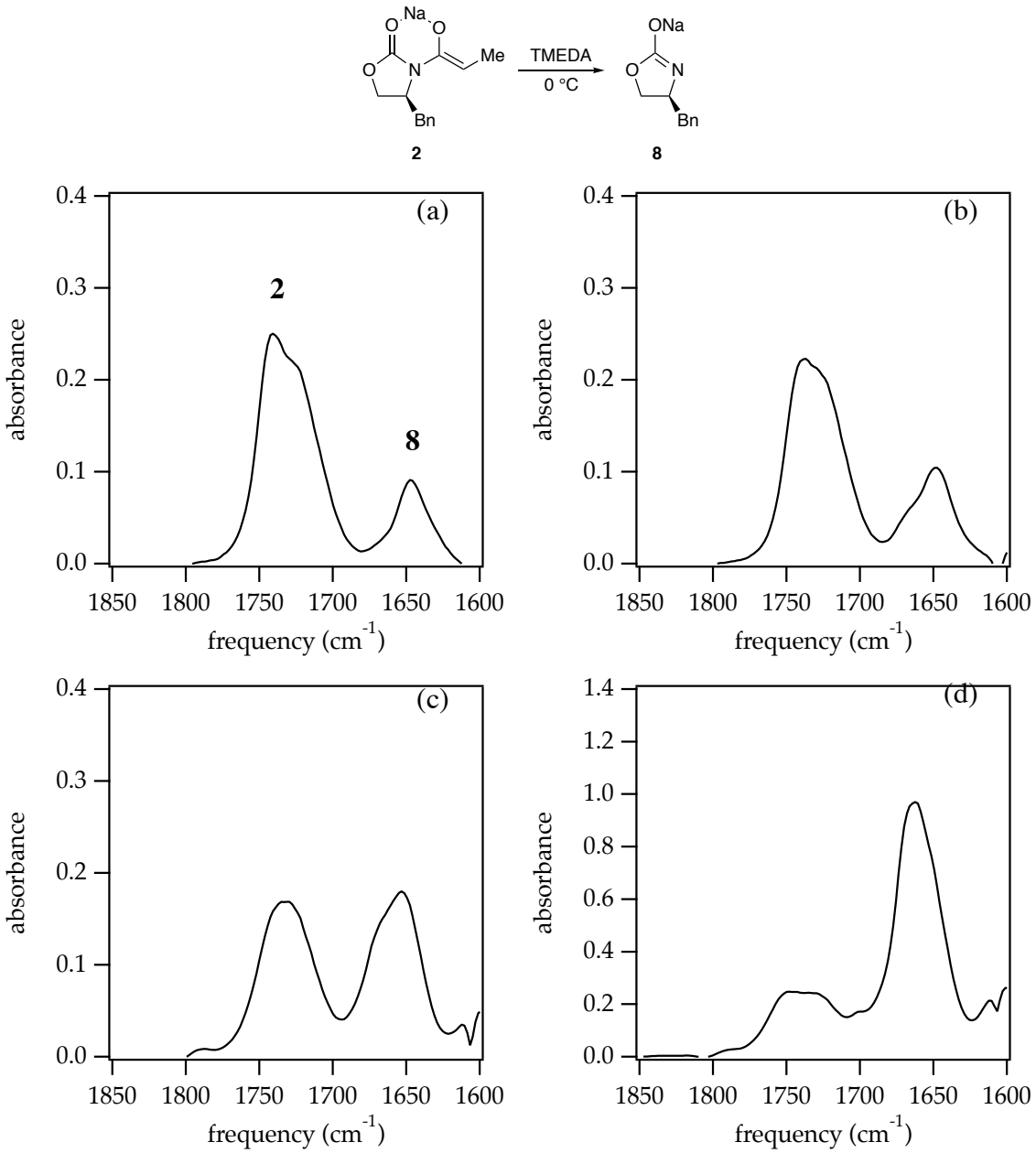


Figure A.2.3. IR spectrum of 0.10 M **8** in 1.0 M TMEDA/toluene recorded at –78 °C.


Na
O
O
O
N
Me
Bn
TMEDA
0 °C
ONa
O
N
Bn
2
8
(a)
(b)
(c)
(d)
2
8
absorbance
frequency (cm-1)
0.0
0.1
0.2
0.3
0.4
0.6
0.8
1.0
1.2
1.4
1850
1800
1750
1700
1650
1600

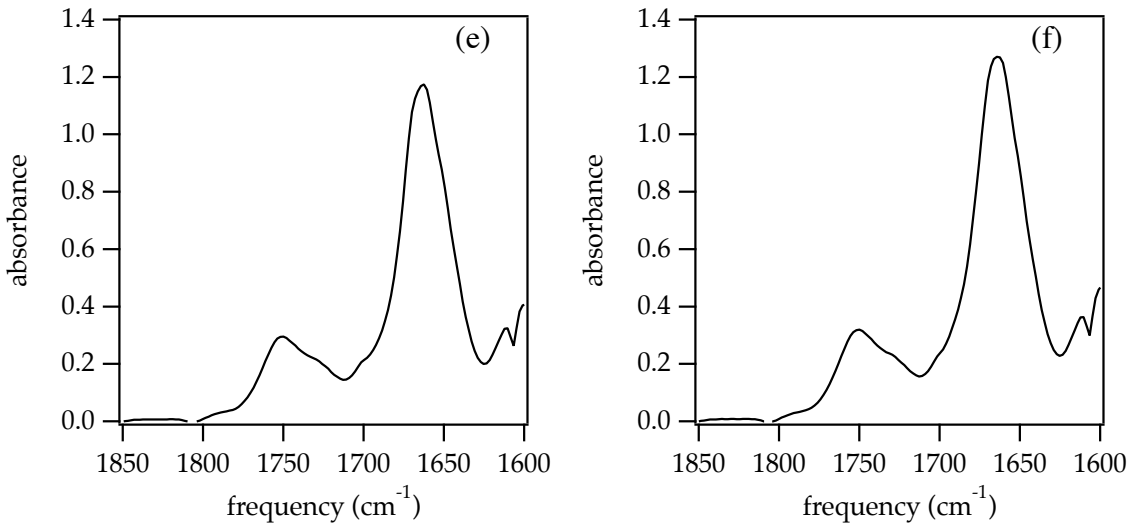


Figure A.2.4. IR spectra of 0.10 M **2** and 0.050 M NaHMDS in 1.0 M TMEDA/toluene recorded at 0 °C after (a) 1 min; (b) 15 min; (c) 45 min; (d) 1.5 h; (e) 2.5 h; (f) 4 h. Nearly instantaneous enolate formation is followed by decomposition to give deacylated product **8**.

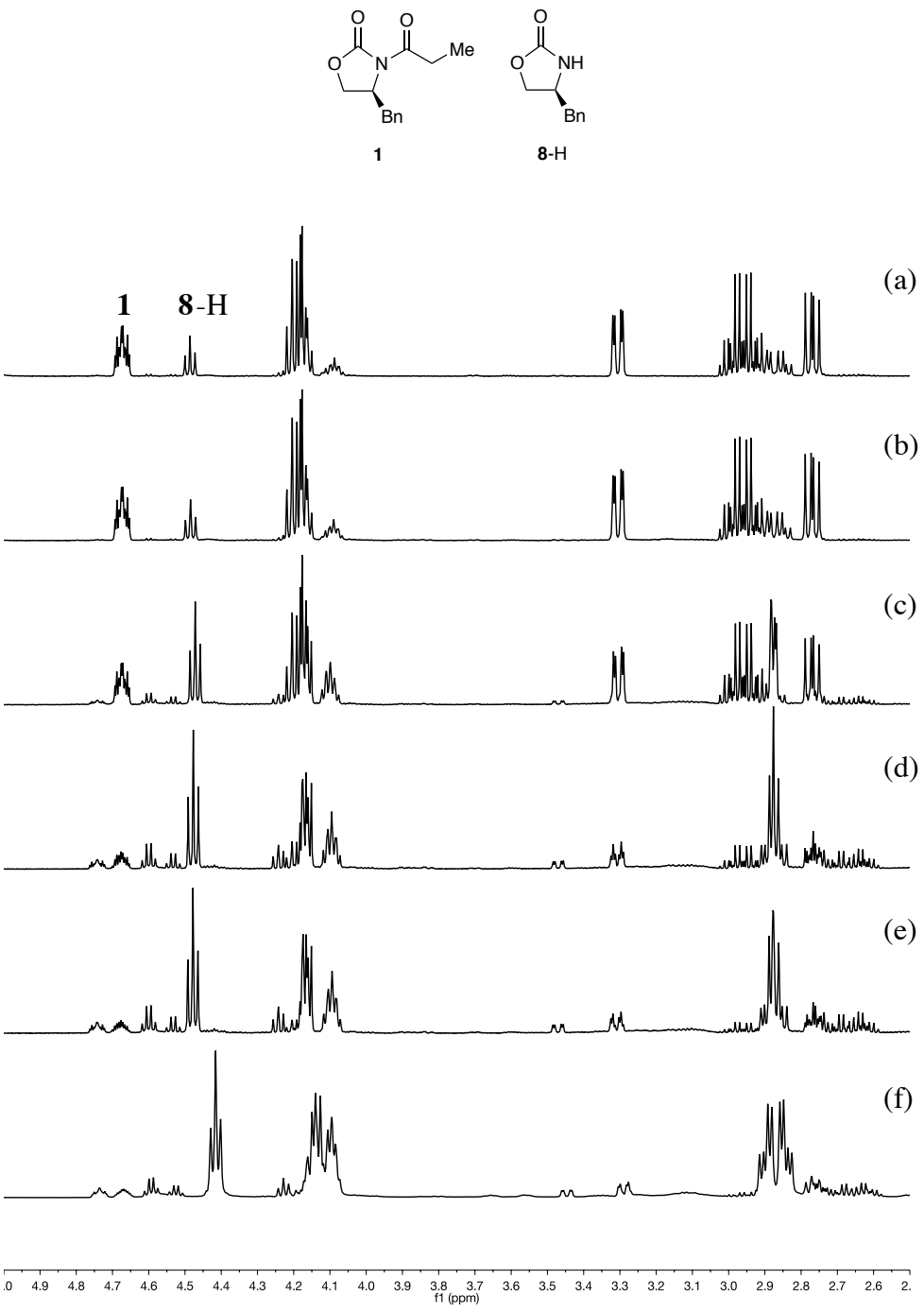


Figure A.2.5. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 °C of 0.10 M **2** and 0.050 M NaHMDS in 1.0 M TMEDA/toluene quenched with HCl (conc.), after aging at 0 °C for: (a) 1 min; (b) 15 min; (c) 45 min; (d) 1.5 h; (e) 2.5 h; (f) 4 h. Spectra show quenched enolate (starting material **1**) is gradually converted into quenched decomposition product (deacylated oxazolidinone).

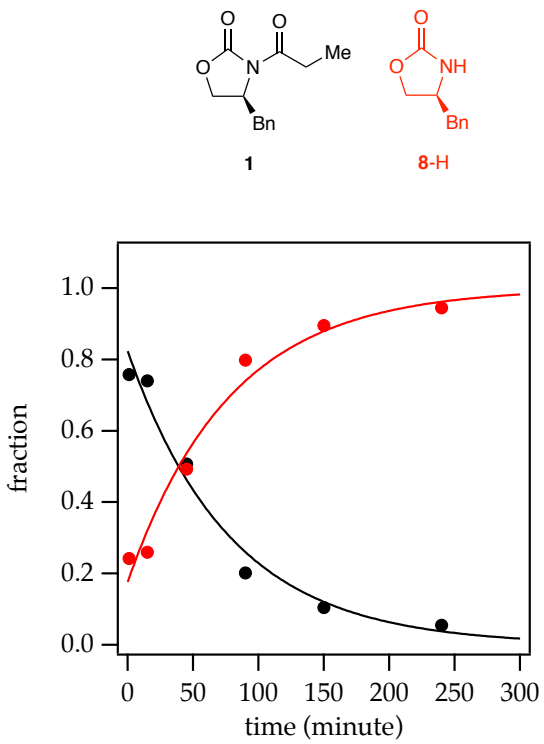


Figure A.2.6. Plot of the fraction of **1** in quenched samples of enolate **2** versus time of aging at 25 °C. $y = a * e^{-bx}$, $a = 0.98 \pm 0.03$, $b = 0.016 \pm 0.001$.

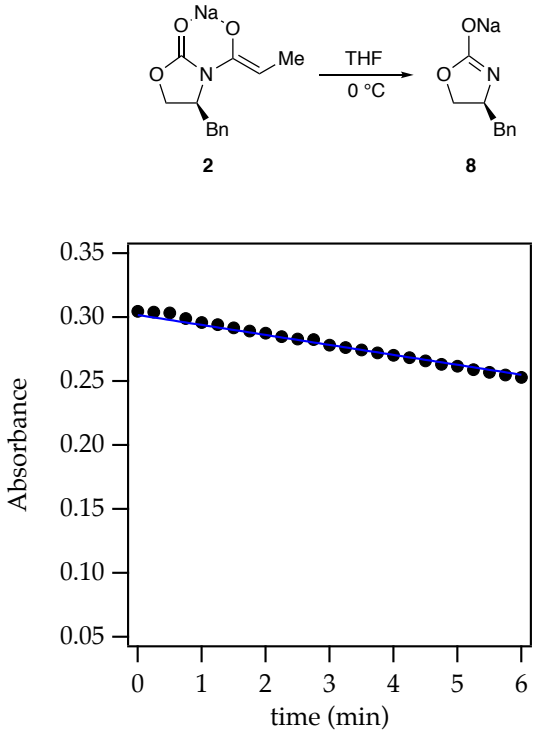


Figure A.2.7. Plot showing loss of enolate **2** (0.10 M) with 0.050 M excess NaHMDS in THF at 0 °C. $y = a * (1 + bx)$, $a = 0.3017 \pm 0.0004$, $b = 0.0258 \pm 0.0001$. Decomposition of enolate **2** in THF is faster than in TMEDA/toluene ($k_{THF/TMEDA} = 1.6$).

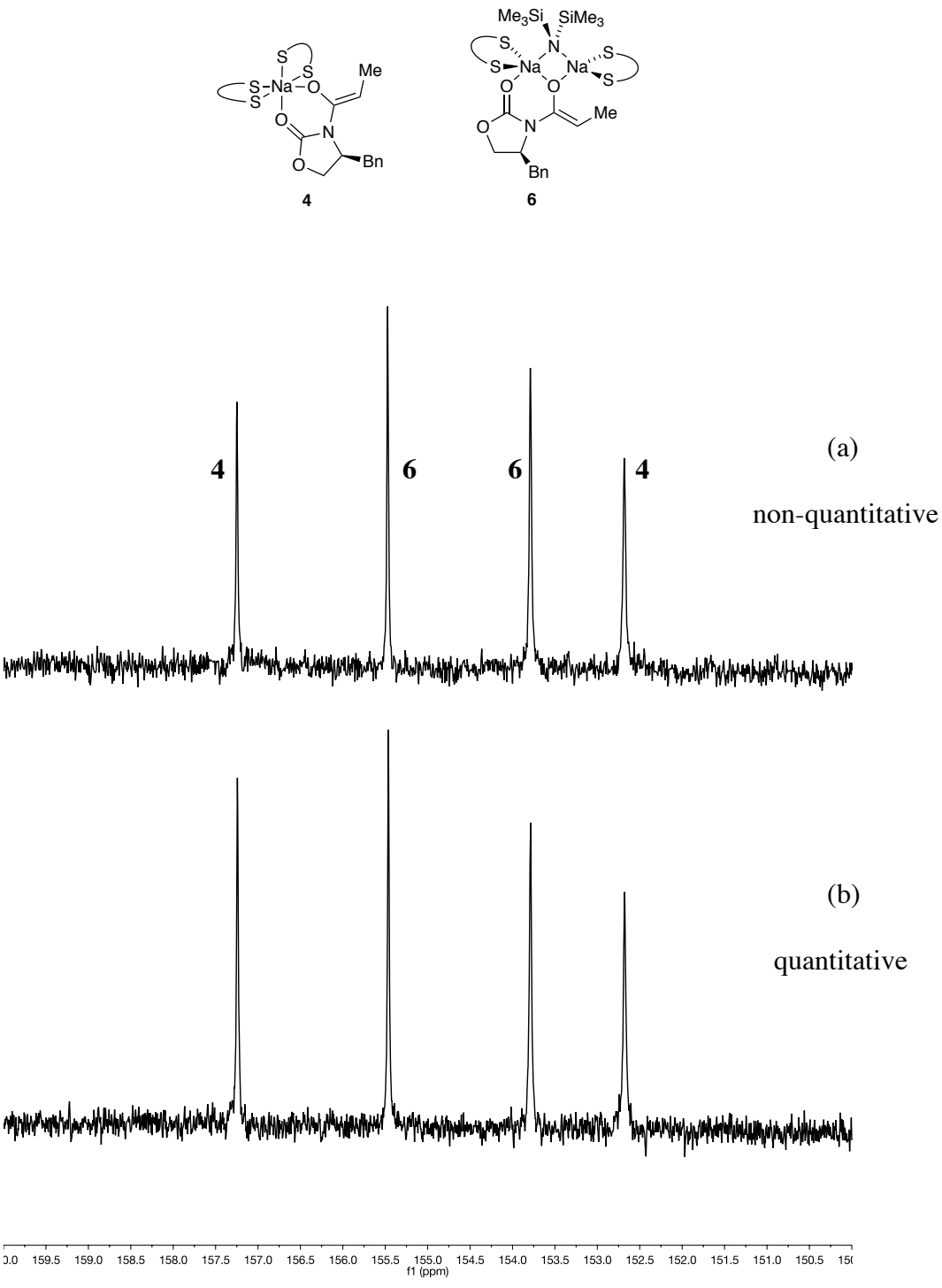


Figure A.2.8. ^{13}C NMR spectra of 0.20 M **4** and 0.10 M NaHMDS in 1.0 M TMEDA/toluene recorded at –80 °C. The qualitative spectrum (a) is acquired with 1.0 s relaxation delay and 11.75 pulse width. The quantitated spectrum is acquired with 30 s. relaxation delay and 22 pulse width. The experiment shows the integrations are ±<10%.

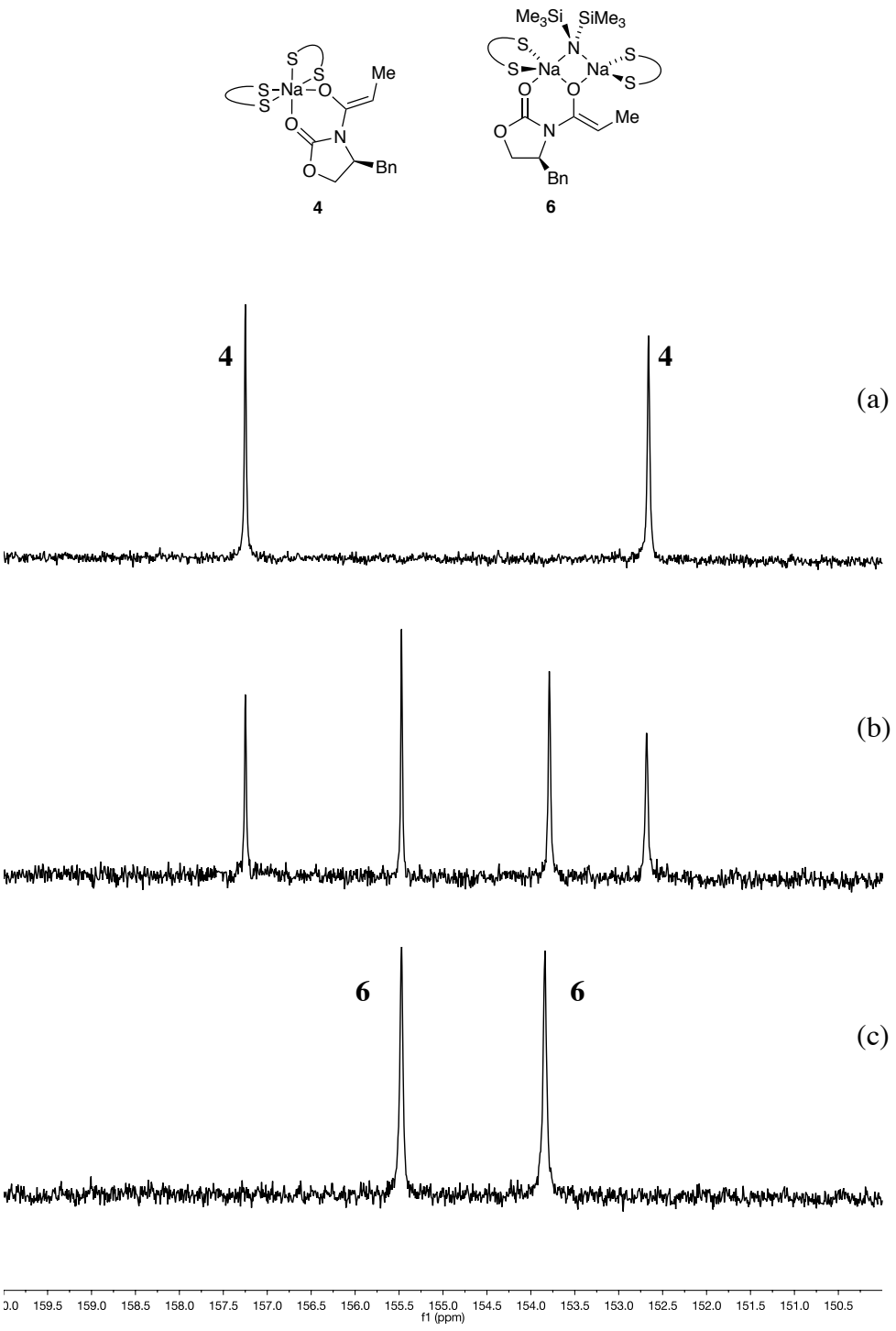


Figure A.2.9. ^{13}C NMR spectra of 0.20 M **4** in 1.0 M TMEDA/toluene recorded at –80 °C with (a) no NaHMDS; (b) 0.10 M NaHMDS; (c) 0.20 M NaHMDS. The experiment shows enolate **2** is converted quantitatively to mixed aggregate **6**

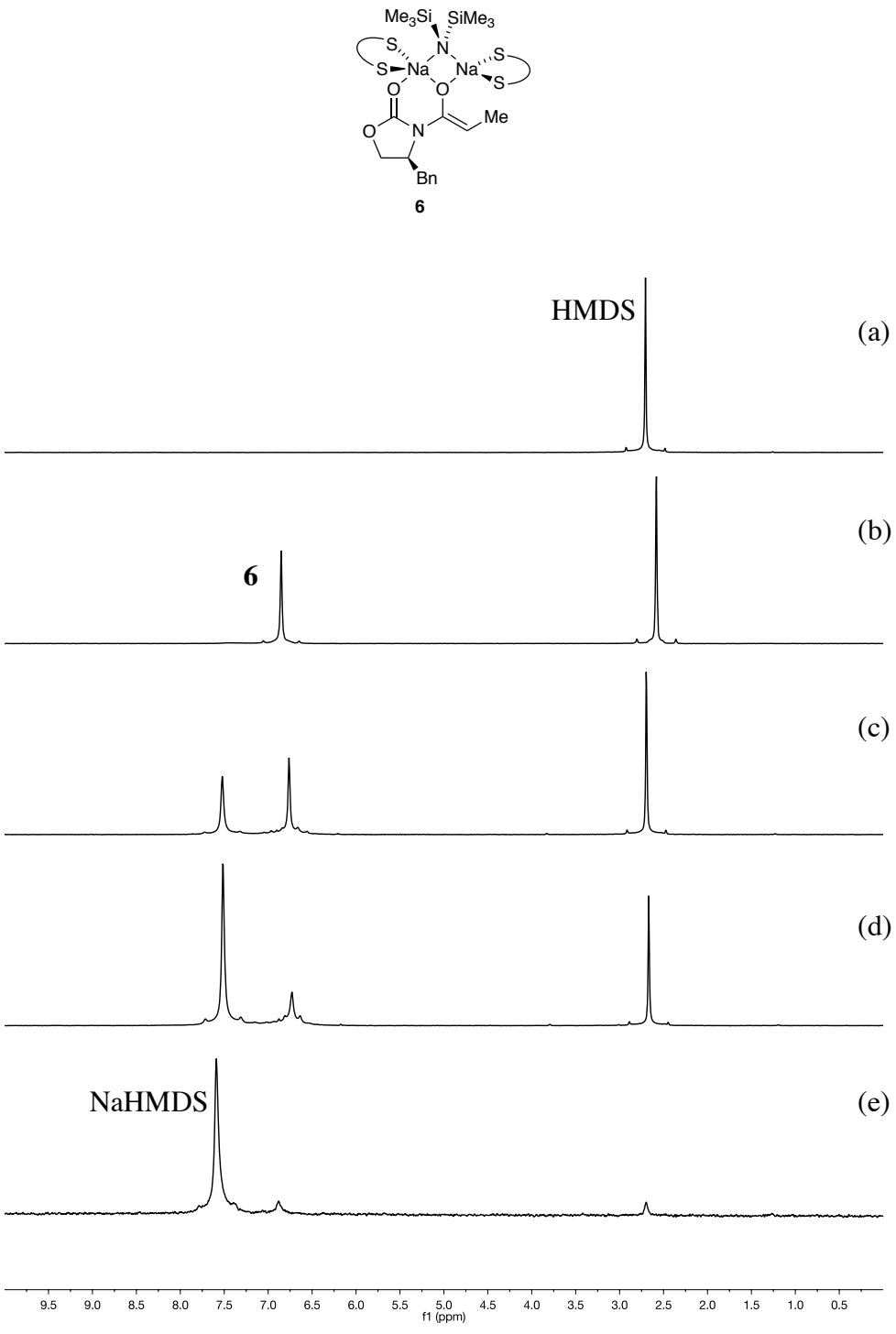


Figure A.2.10. ^{13}C NMR spectra of 0.20 M **4** in 1.0 M TMEDA/toluene recorded at –80 °C with (a) no excess NaHMDS; (b) 0.20 M excess NaHMDS; (c) 0.40 M excess NaHMDS; (d) 0.80 M NaHMDS; (e) no enolate and 1.0 M NaHMDS. Enolate monomer not shown. HMDS (2.7 ppm), NaHMDS (7.6 ppm) and mixed aggregate **6** (6.9 ppm, TMS carbon) are as labeled.

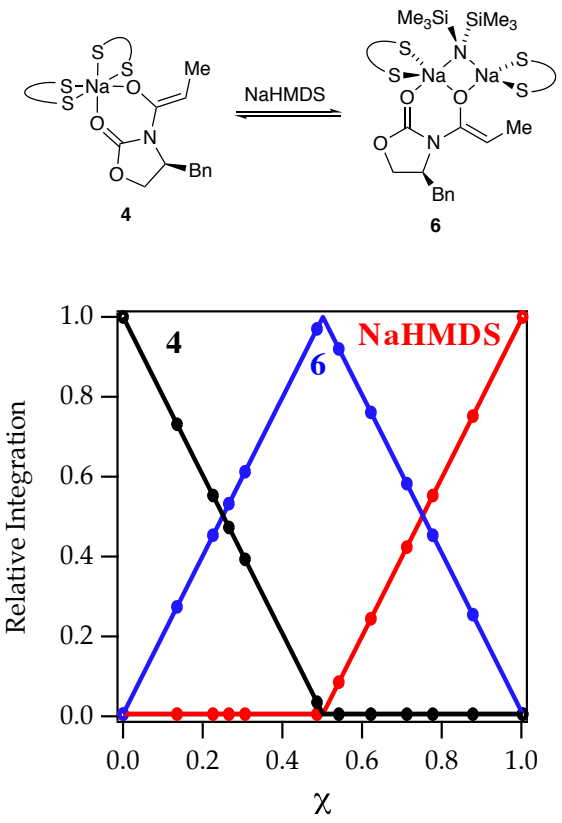


Figure A.2.11. Job plot showing the relative integrations versus the measured mole fraction of NaHMDS, χ_{NaHMDS}, in mixtures of NaHMDS and enolate **4** (0.30 M total titer) in 0.60 M TMEDA/toluene recorded at −80 °C. The curves represent a parametric fit to a dimer-based model.

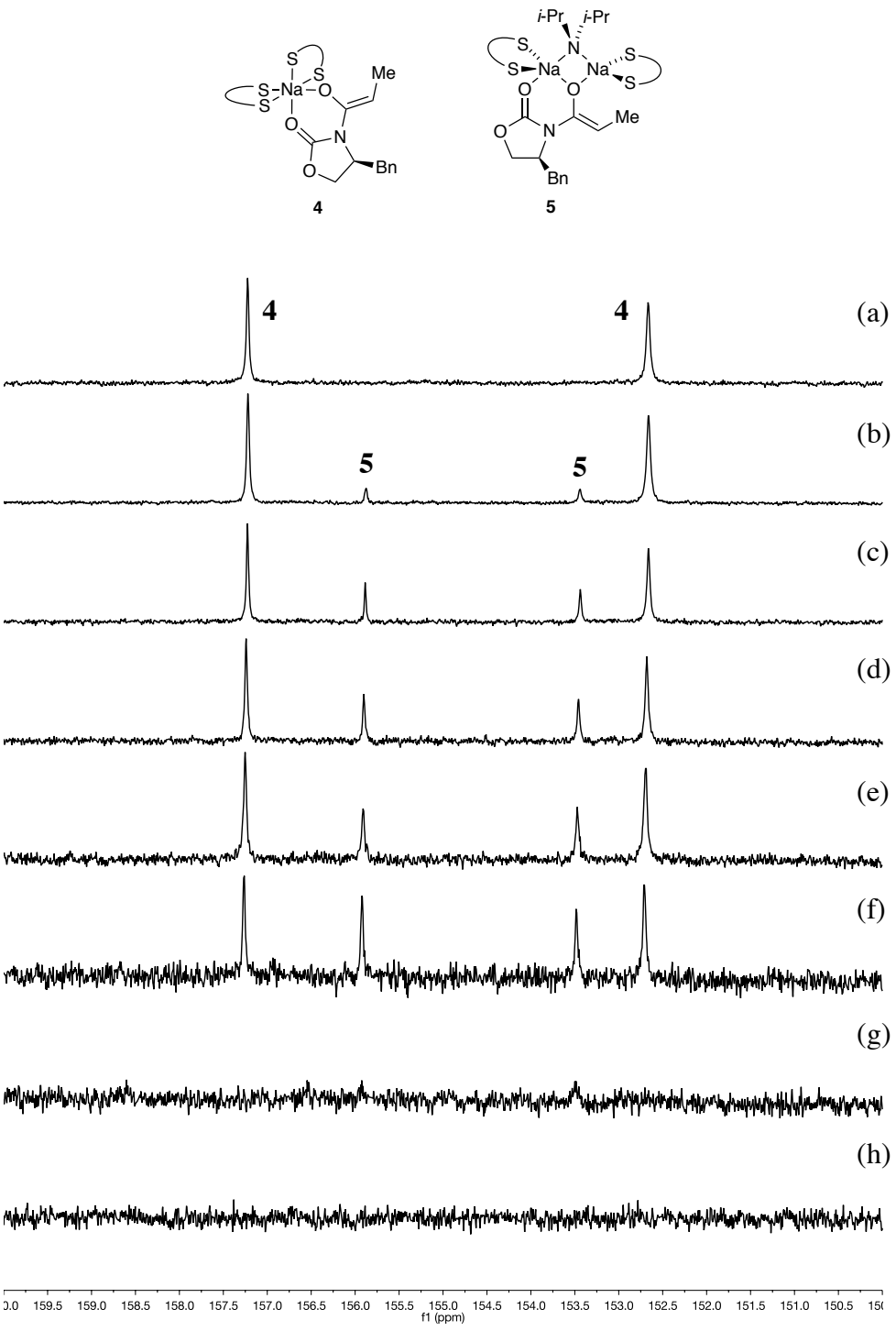
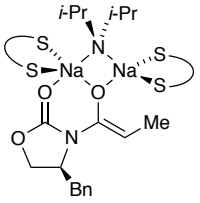


Figure A.2.12. ^{13}C NMR spectra of enolate **4** and NaDA (0.40 M total titer) in 1.0 M TMEDA/toluene recorded at –80 °C. The samples contain (a) 0.40 M **4**; (b) 0.35 M **4** and 0.050 M NaDA; (c) 0.30 M **4** and 0.10 M NaDA; (d) 0.25 M **4** and 0.15 M NaDA; (e) 0.20 M **4** and 0.20 M NaDA; (f) 0.15 M **4** and 0.25 M NaDA; (g) 0.10 M **4** and 0.30 M NaDA; (h) 0.050 M **4** and 0.35 M NaDA.



5

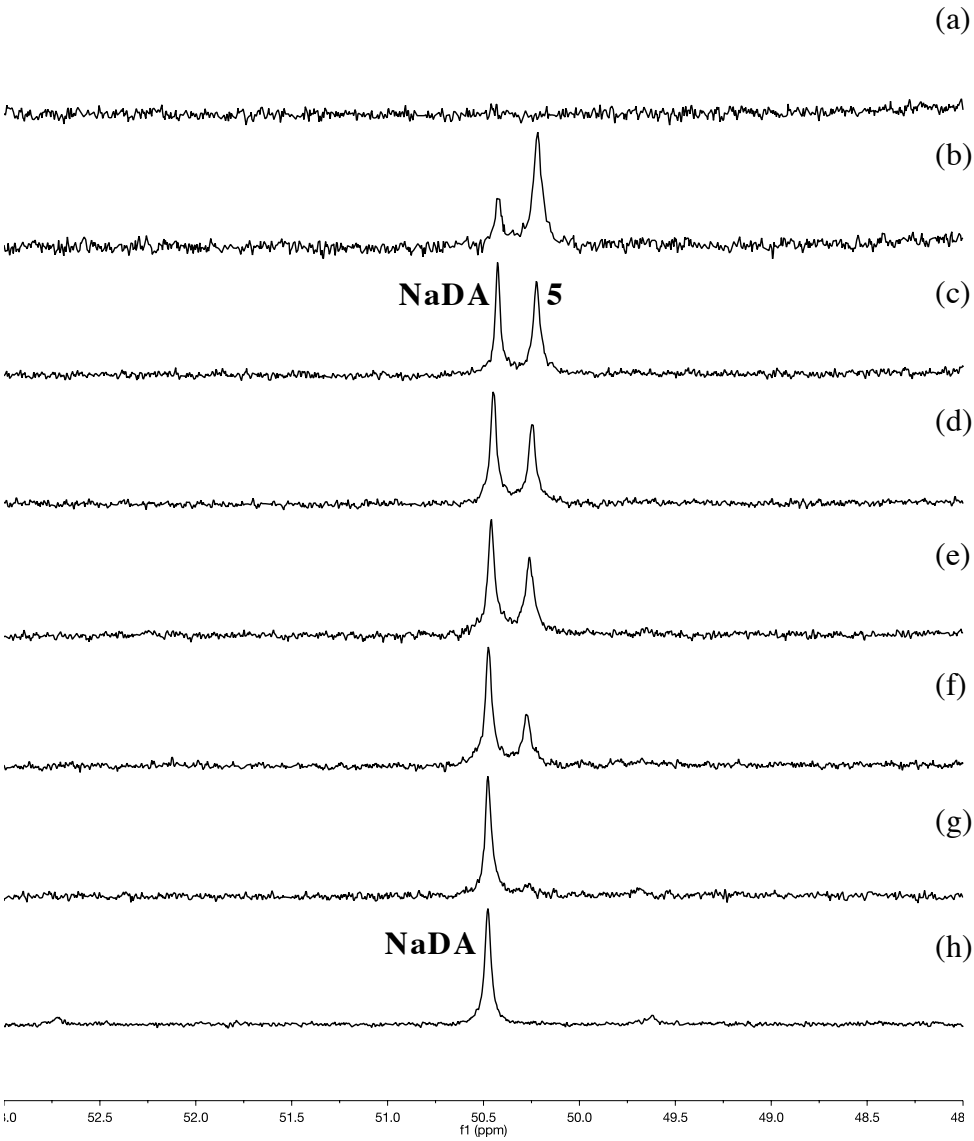


Figure A.2.13. ^{13}C NMR spectra of enolate **4** and NaDA (0.40 M total titer) in 1.0 M TMEDA/toluene recorded at –80 °C. The samples contain (a) 0.40 M **4**; (b) 0.35 M **4** and 0.050 M NaDA; (c) 0.30 M **4** and 0.10 M NaDA; (d) 0.25 M **4** and 0.15 M NaDA; (e) 0.20 M **4** and 0.20 M NaDA; (f) 0.15 M **4** and 0.25 M NaDA; (g) 0.10 M **4** and 0.30 M NaDA; (h) 0.050 M **4** and 0.35 M NaDA. Free and bound NaDA (methine carbon) are illustrated.

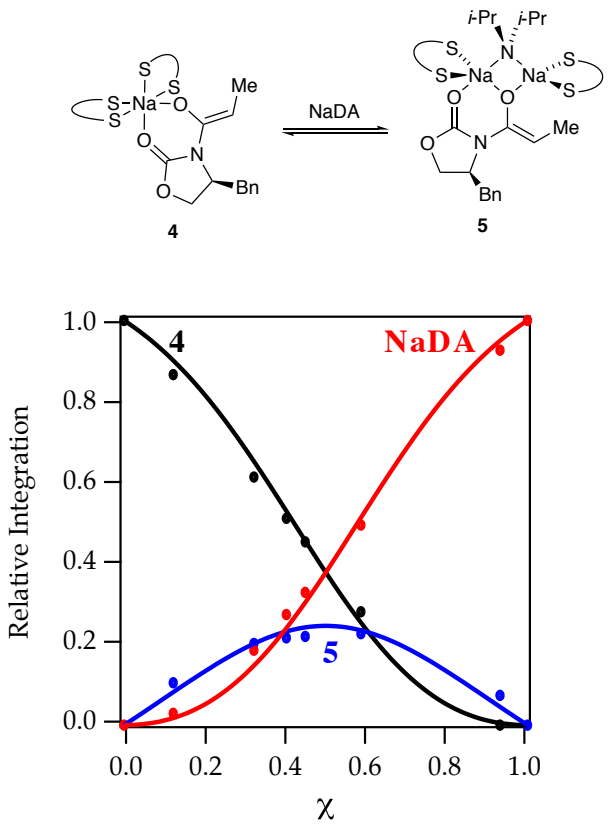


Figure A.2.14. Job plot showing the relative integrations versus the measured mole fraction of NaDA, χ_{NaDA}, for mixtures of NaDA and enolate **4** (0.40 M total titer) in 1.0 M TMEDA/toluene recorded at −80 °C. The data comes from Figures A.2.12 and A.2.13.

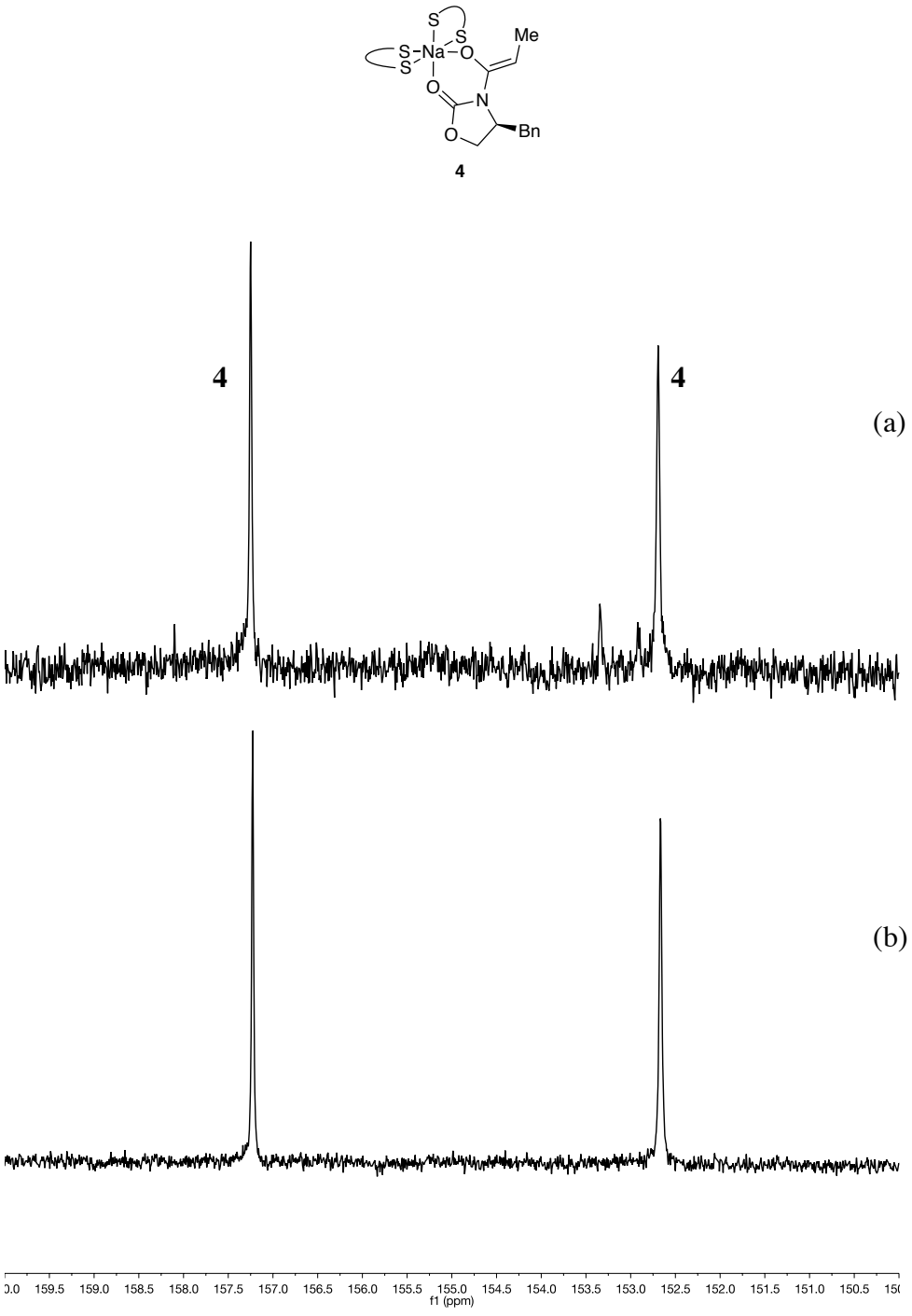


Figure A.2.15. ^{13}C NMR spectra of enolate **4** (0.20 M) in 1.0 M TMEDA/toluene recorded at –80 °C generated from (a) 0.20 M NaHMDS; (b) 0.20 M NaDA. The experiment shows the spectrum of **4** is base independent.

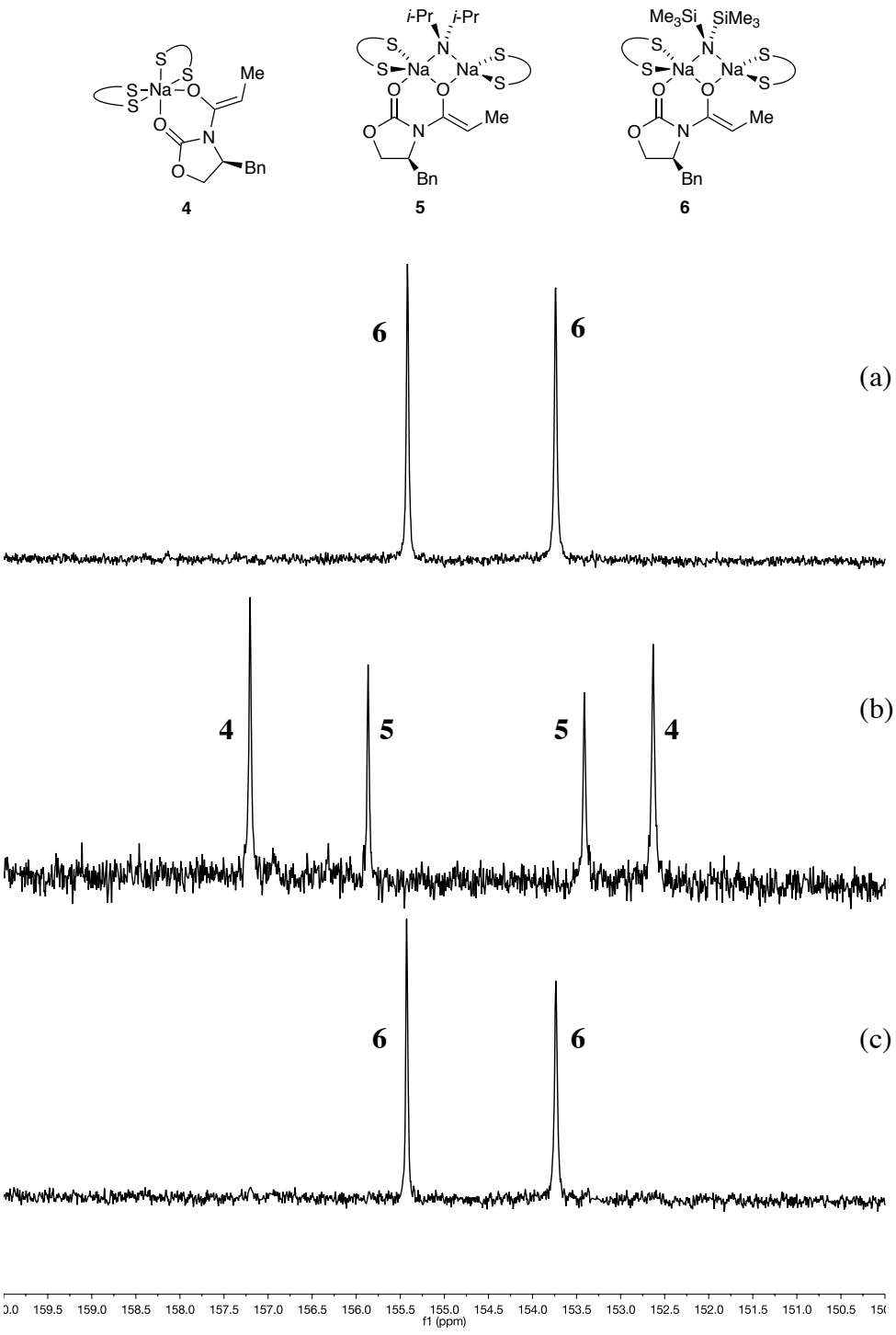


Figure A.2.16. ^{13}C NMR spectra in 1.0 M TMEDA/toluene at –80 °C of (a) 0.20 M **6**; (b) 0.20 M NaDA and 0.20 M **4**; (c) 0.20 M NaHMDS, 0.20 M NaDA and 0.20 M **4**. The experiment shows NaHMDS forms mixed dimer **6** quantitatively whereas NaDA mixed dimer **5** non-quanitatively. Spectrum (c) shows a competition of NaDA and NaHMDS affords only the NaHMDS-derived mixed dimer **6**.

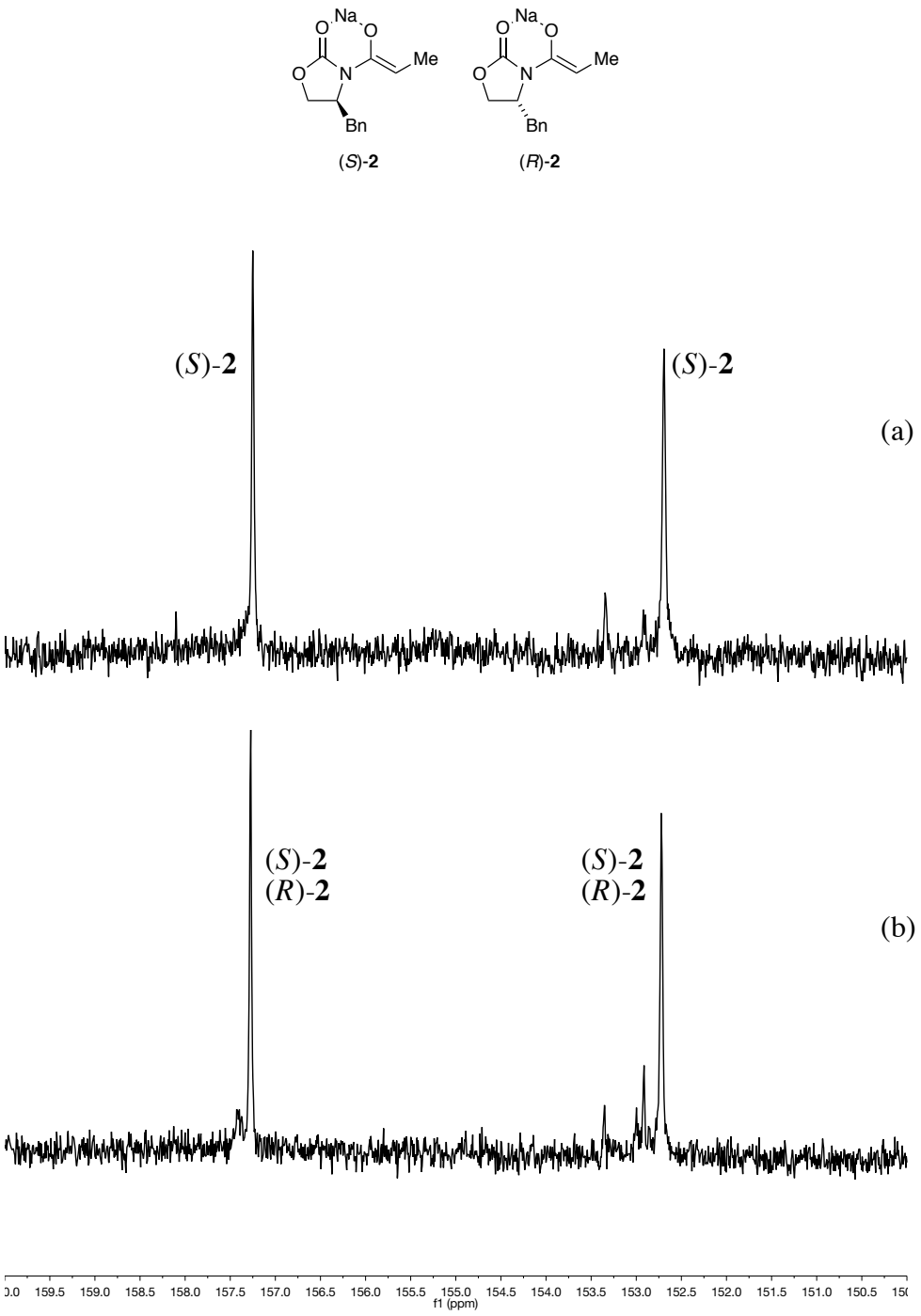


Figure A.2.17. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**; (b) 0.10 M (*R*)-**2** and 0.10 M (*S*)-**2** showing no new resonances that would evidence a heteroaggregate.

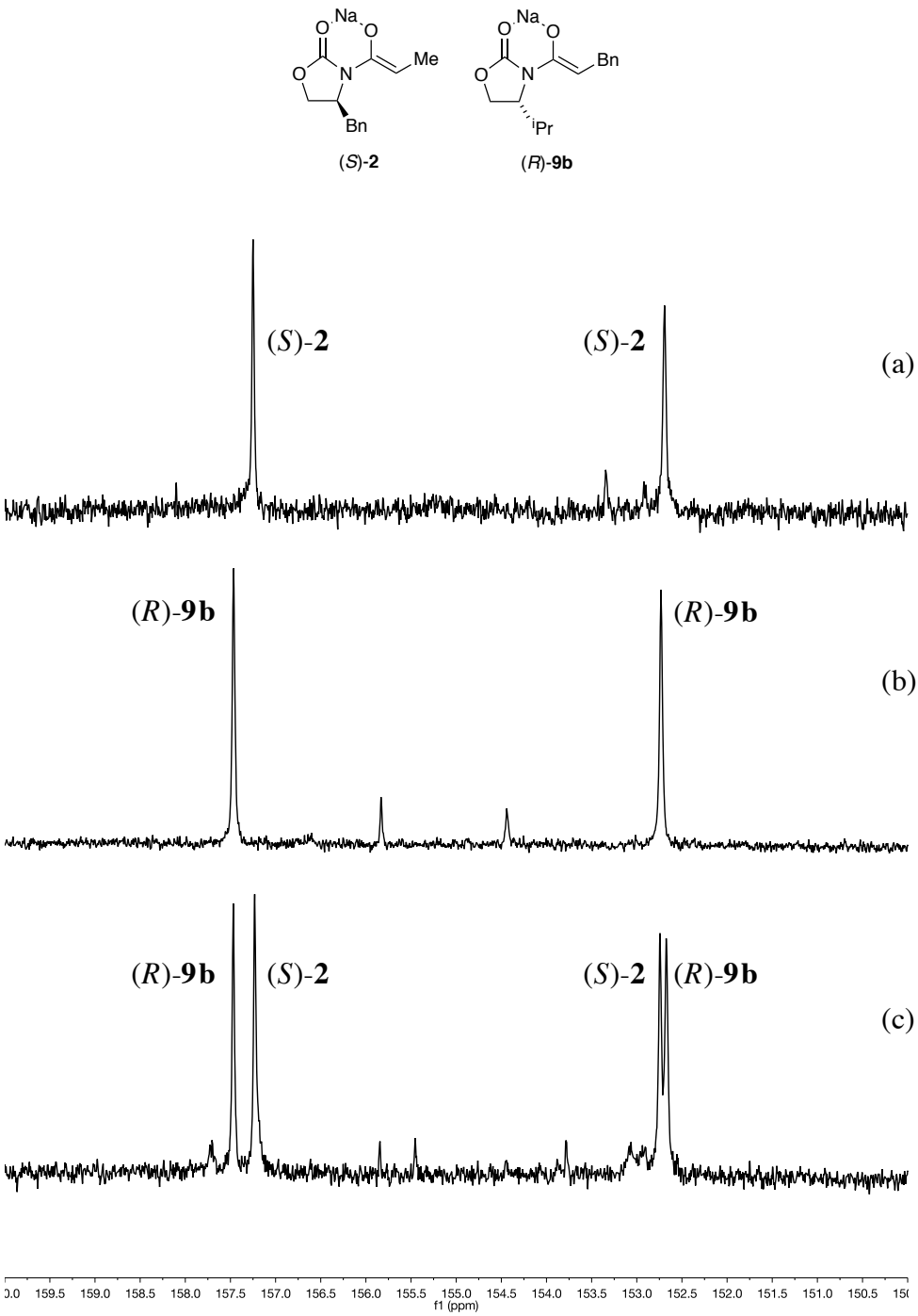


Figure A.2.18. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**; (b) 0.20 M (*R*)-**9b**; (c) 0.10 M (*S*)-**2** and 0.10 M (*R*)-**9b** showing no substantial resonances that would evidence a heteroaggregate.

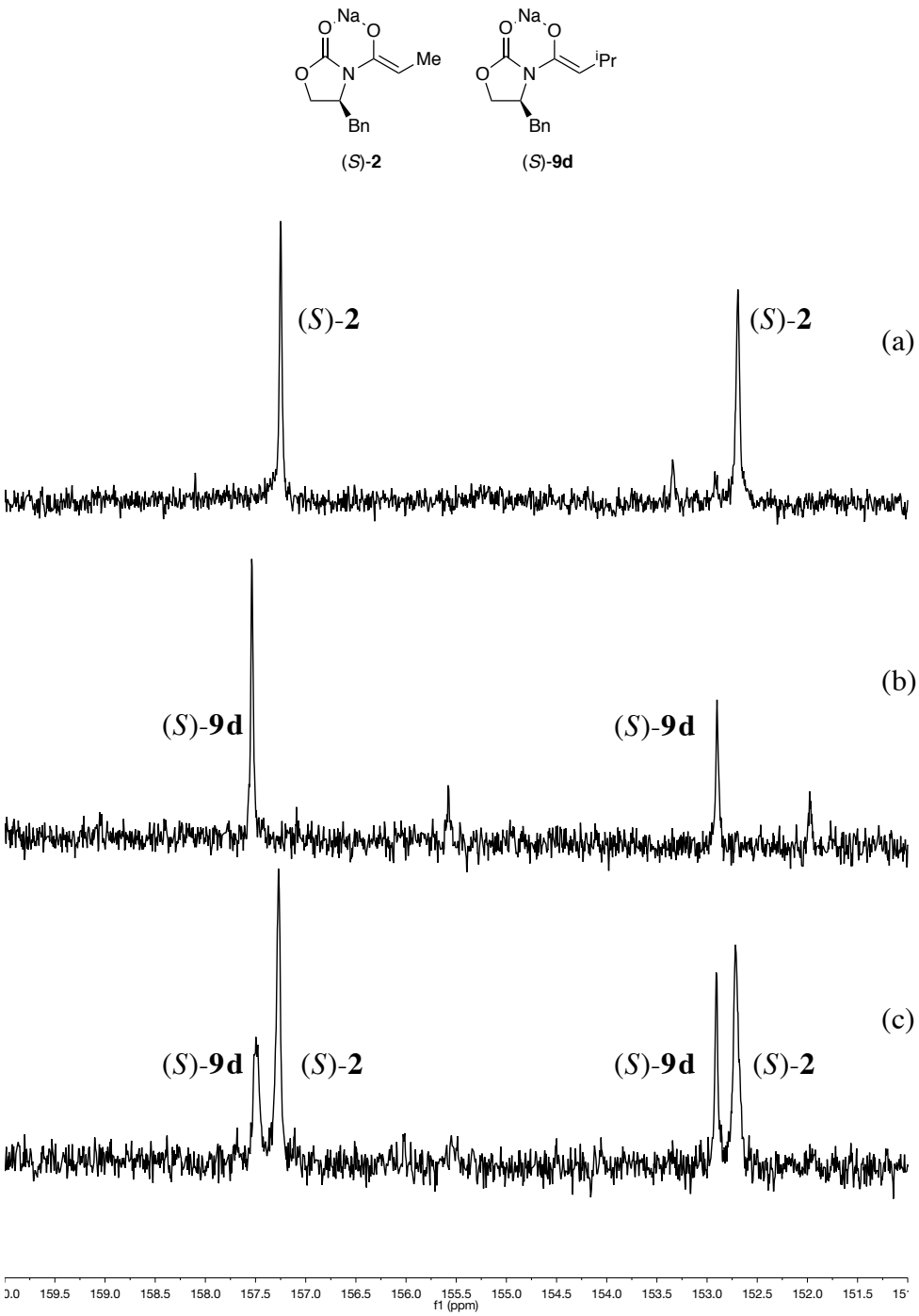


Figure A.2.19. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**; (b) 0.20 M (*S*)-**9d**; (c) 0.10 M (*S*)-**2** and 0.10 M (*S*)-**9d**. No heteroaggregate is observable in (c).

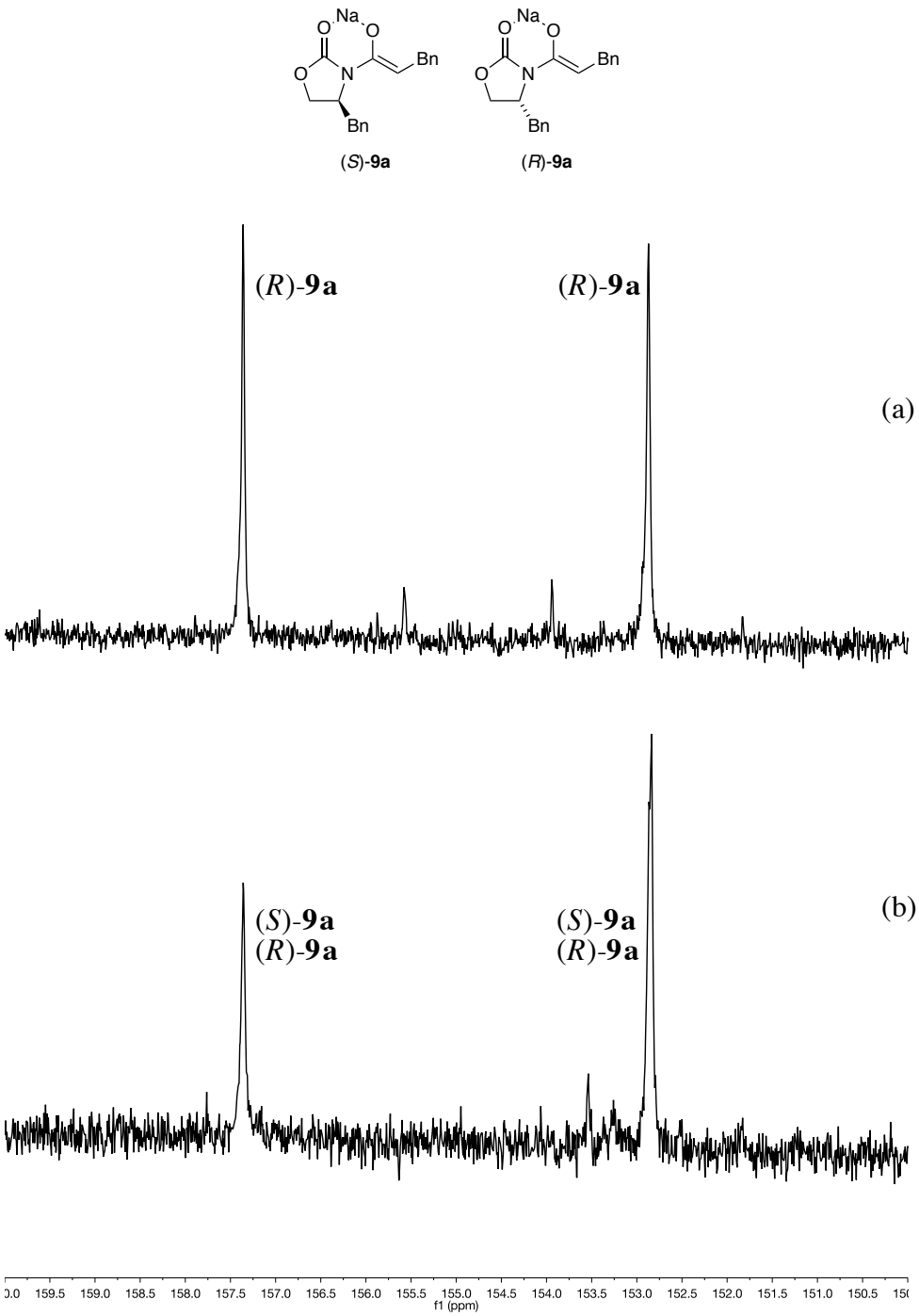


Figure A.2.20. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*R*)-**9a**; (b) 0.10 M (*R*)-**9a** and 0.10 M (*S*)-**9a**. No heteroaggregate is observable in (b).

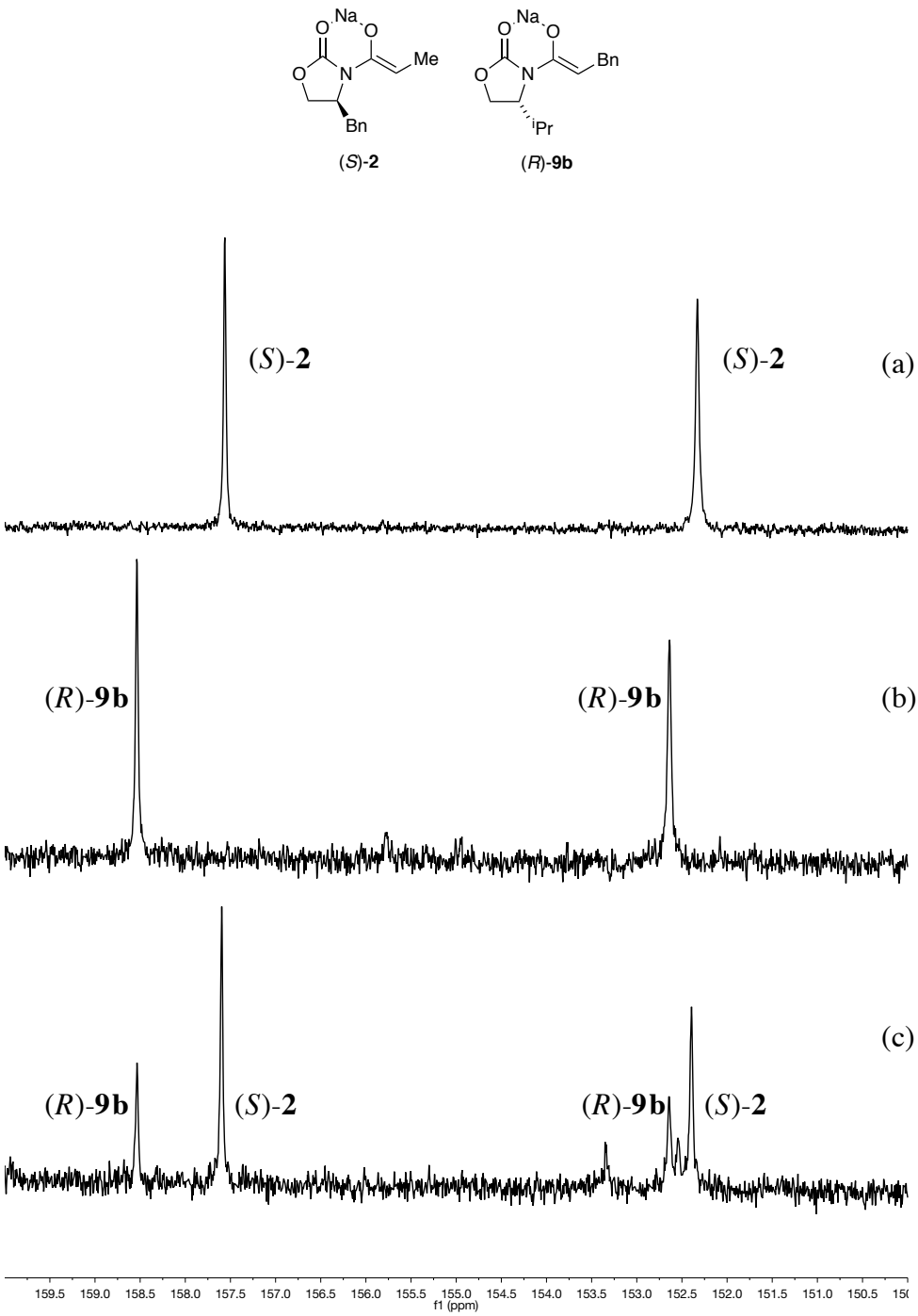


Figure A.2.21. ^{13}C NMR spectra in 1.0 M (*S,S*)-TMCDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**; (b) 0.20 M (*R*)-**9b**; (c) 0.10 M (*S*)-**2** and 0.10 M (*R*)-**9b**.

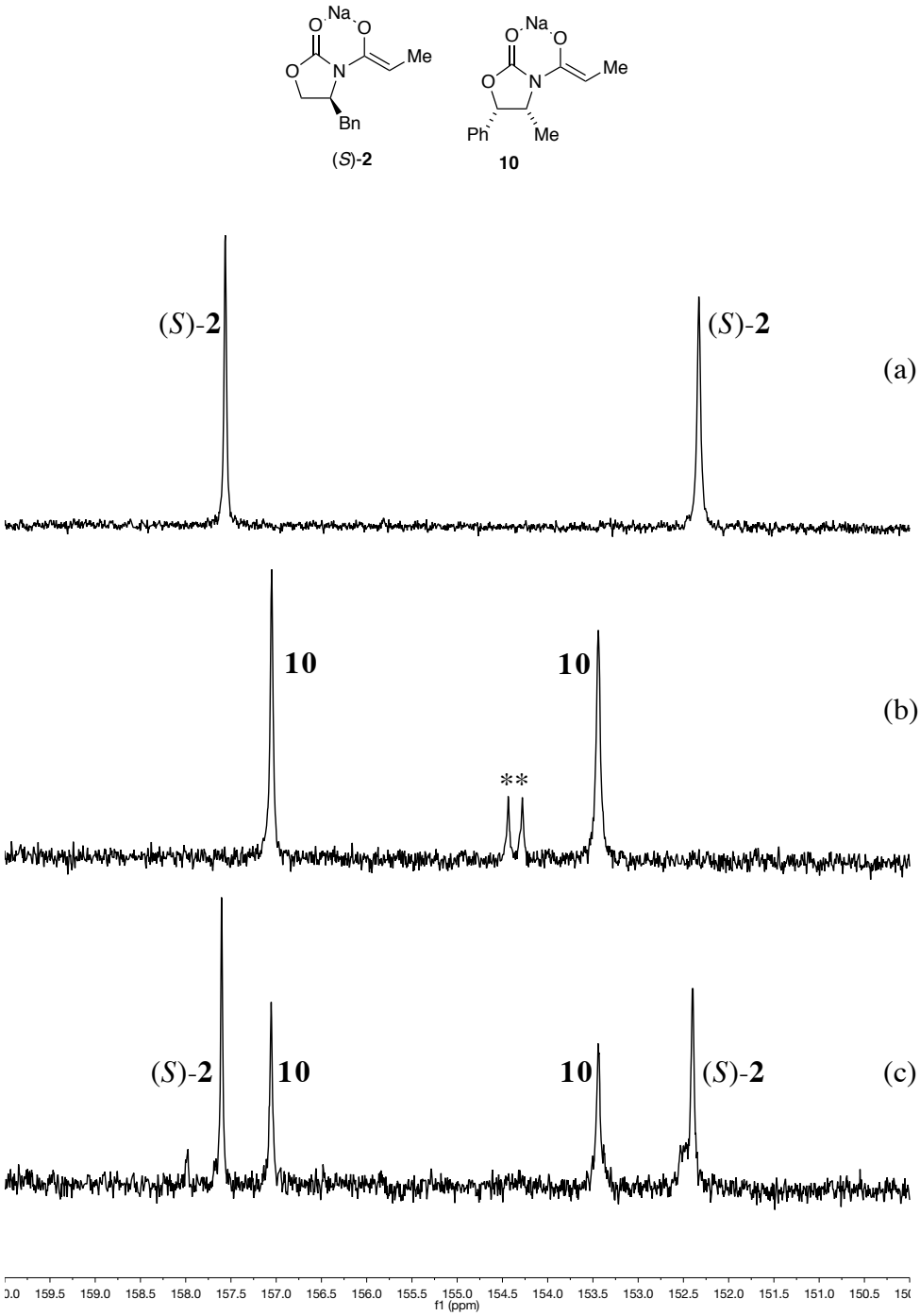


Figure A.2.22. ^{13}C NMR spectra in 1.0 M (*S,S*)-TMCDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**; (b) 0.20 M **10**; (c) 0.10 M (*S*)-**2** and 0.10 M **10**.
***** residual mixed dimer **10**-A is present due to extra NaHMDS remaining.

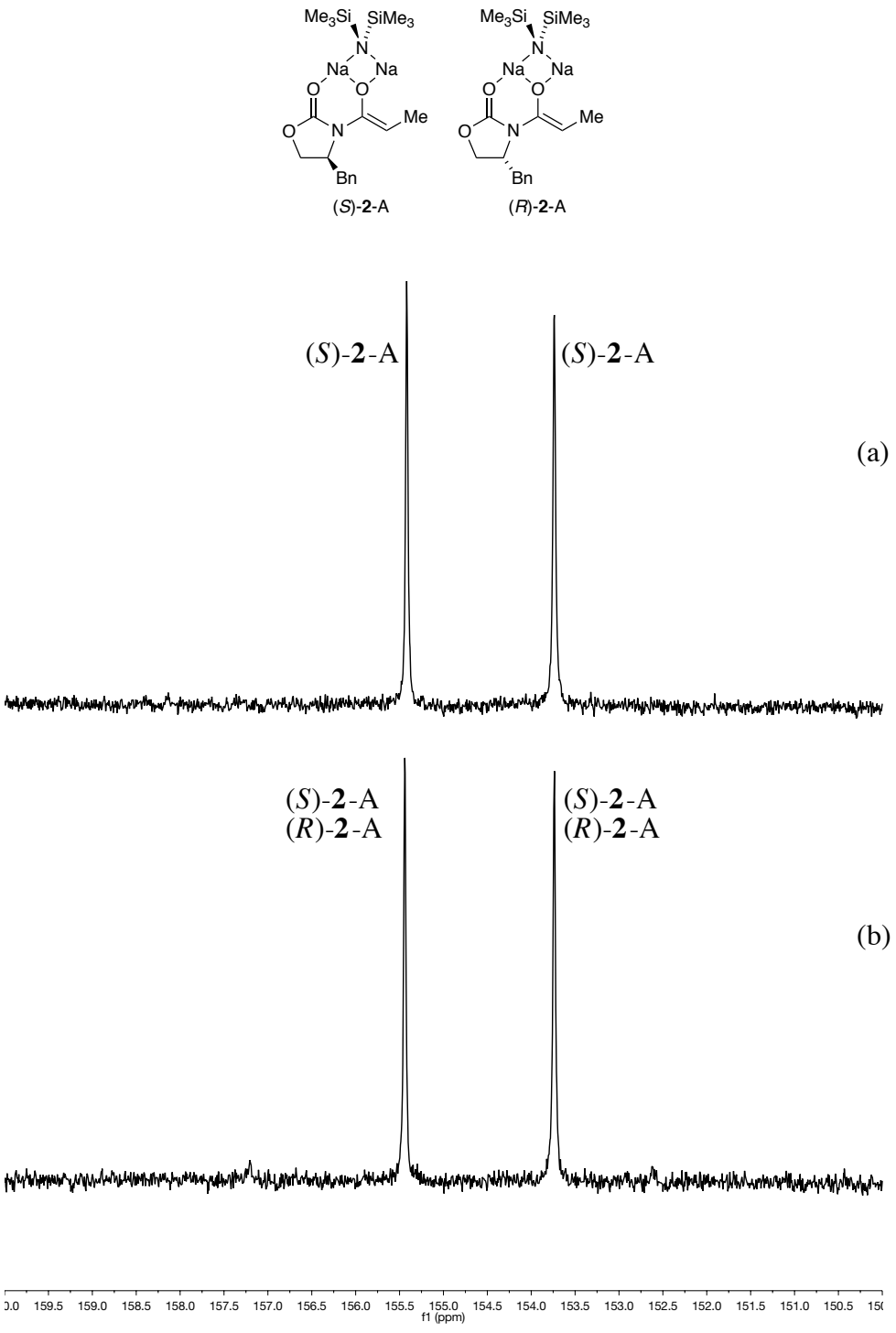


Figure A.2.23. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.10 M (*S*)-**2**-A, 0.10 M (*R*)-**2**-A. Mixing of NaHMDS mixed dimers (*S*)-**2**-A and (*R*)-**2**-A shows no new peak or chemical shift change, consistent with one enolate present in the mixed dimer.

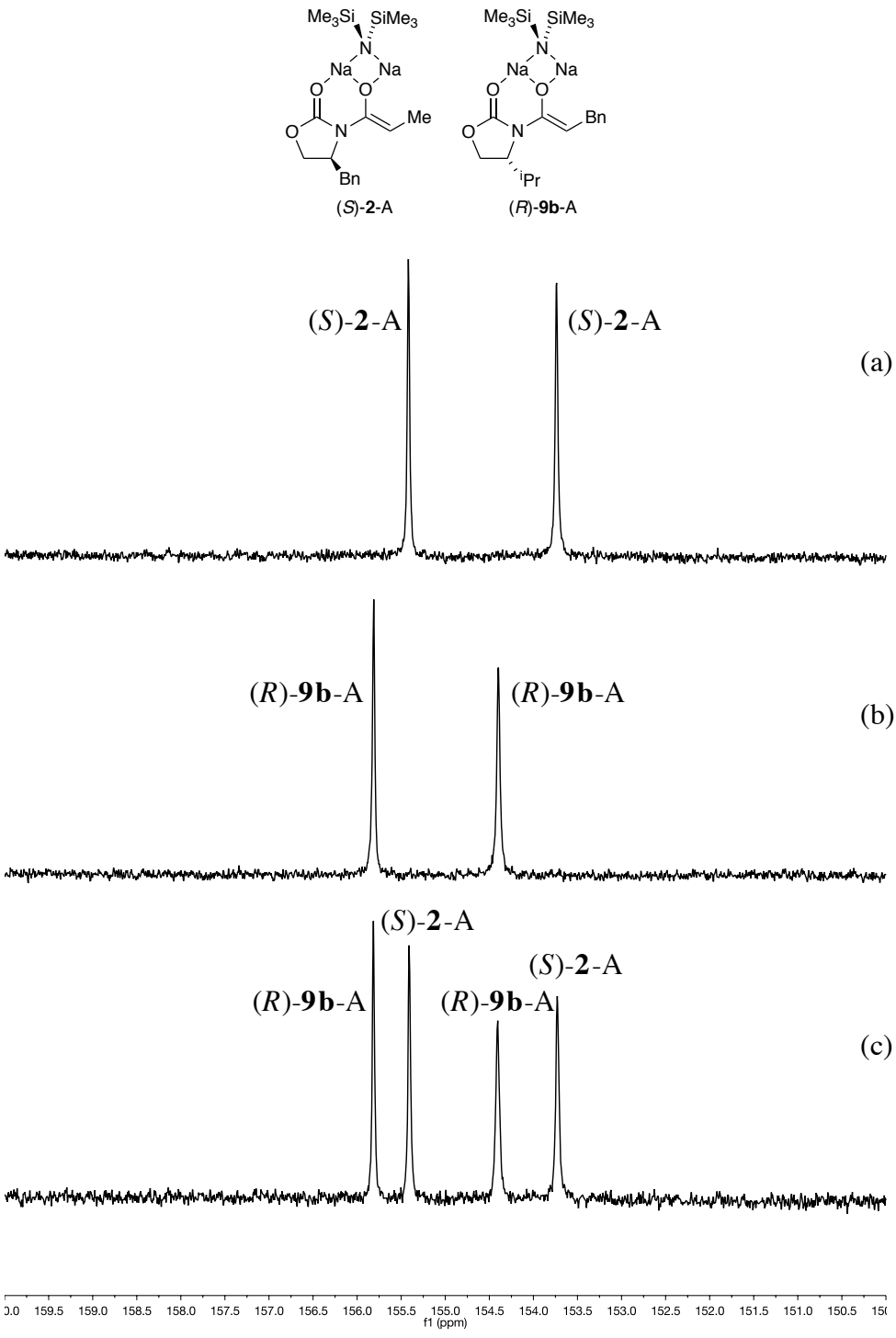


Figure A.2.24. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.20 M (*R*)-**9b**-A; (c) 0.10 M (*S*)-**2**-A, 0.10 M (*R*)-**9b**-A.

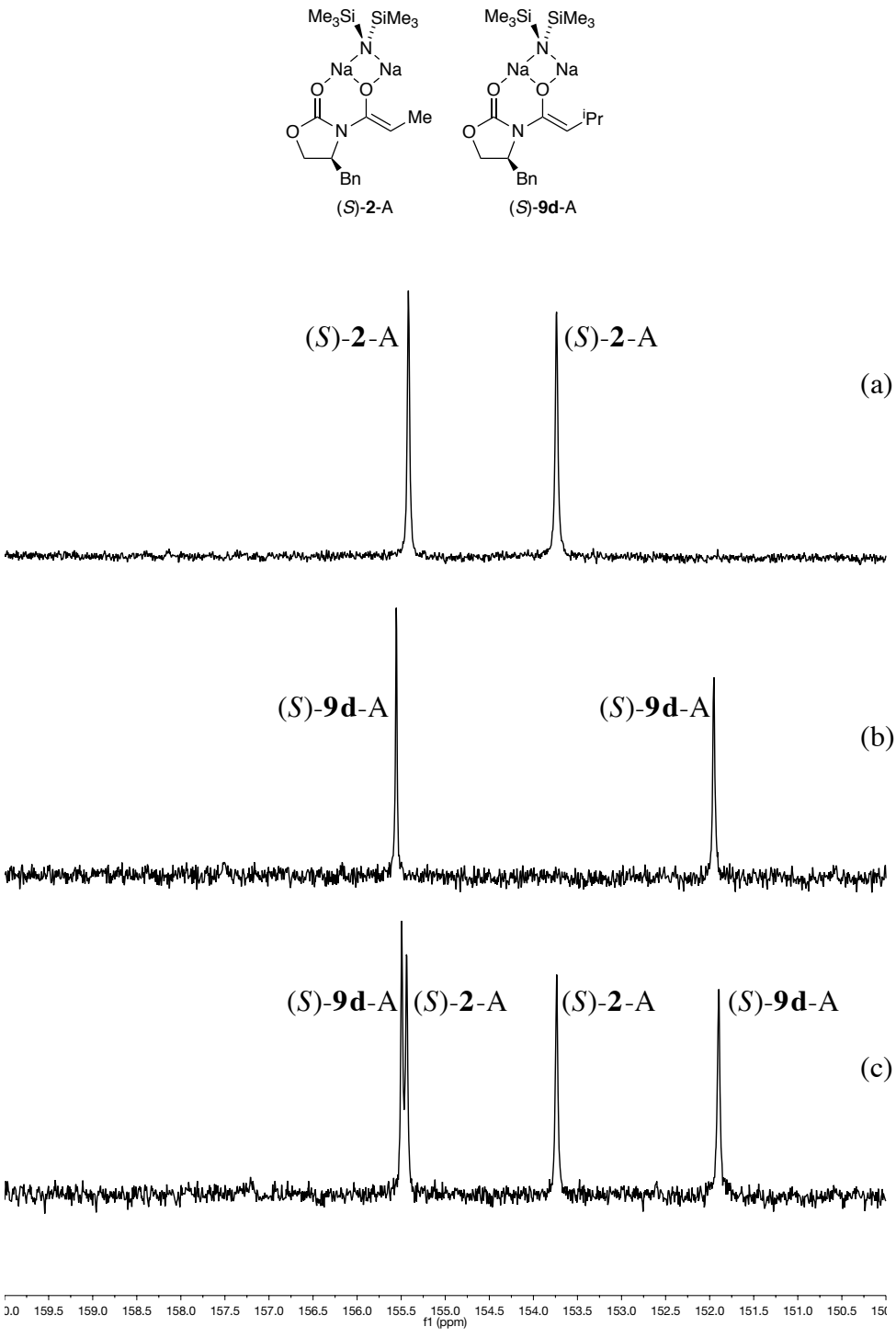


Figure A.2.25. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.20 M (*S*)-**9d**-A; (c) 0.10 M (*S*)-**2**-A, 0.10 M (*S*)-**9d**-A.

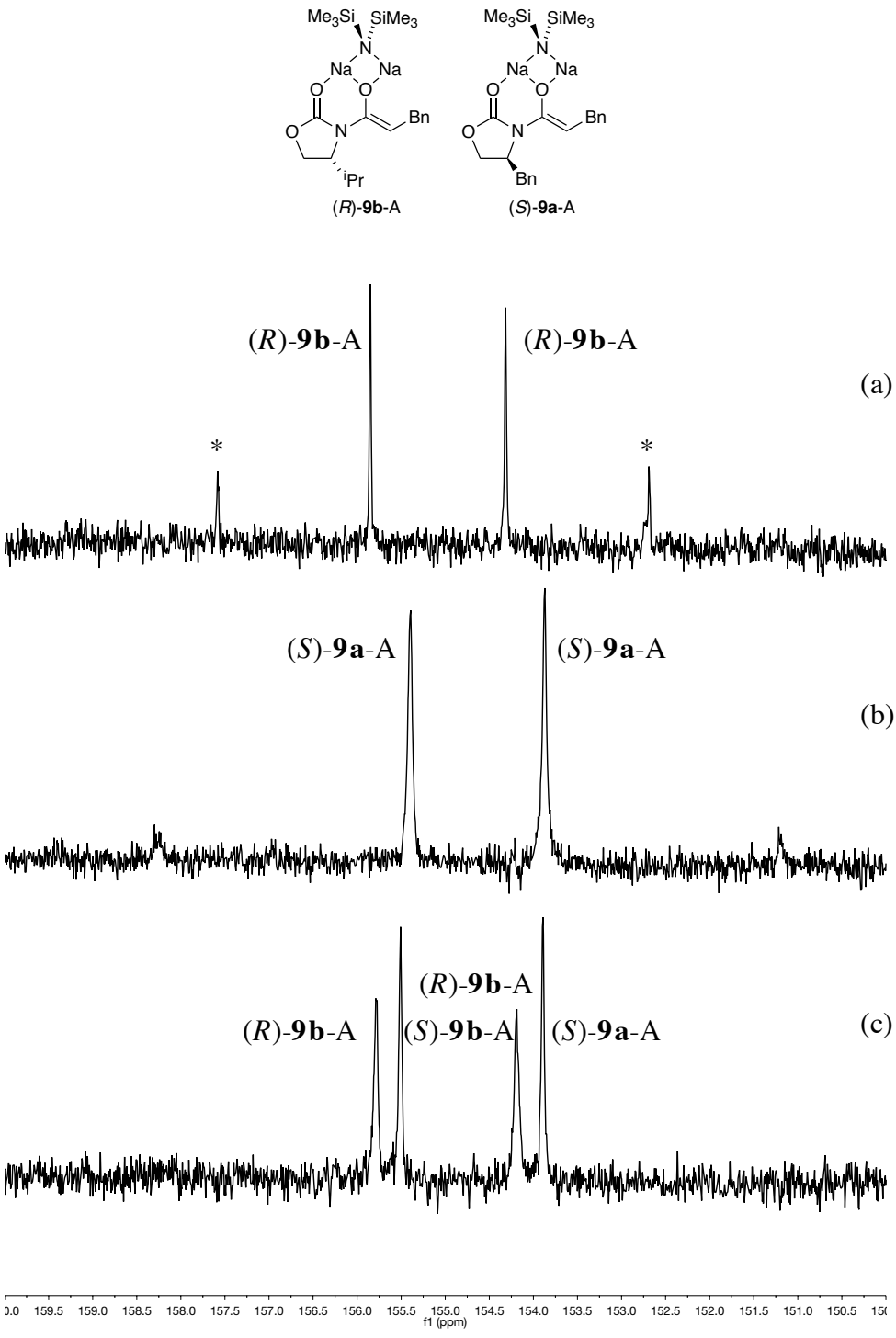


Figure A.2.26. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*R*)-**9b**-A; (b) 0.20 M (*S*)-**9a**-A; (c) 0.10 M (*R*)-**9b**-A, 0.10 M (*S*)-**9a**-A. * homoaggregate residue.

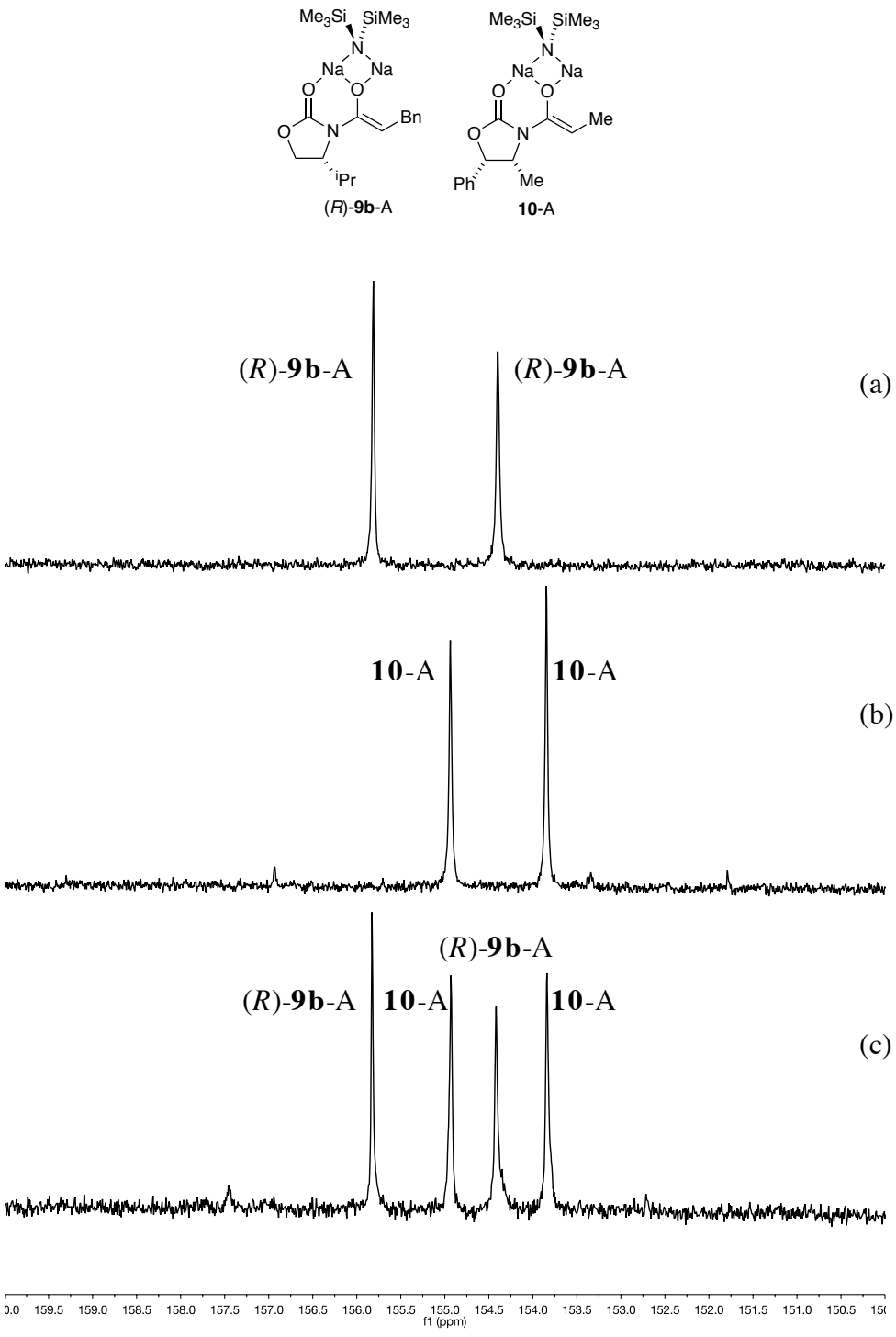


Figure A.2.27. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*R*)-**9b**-A; (b) 0.20 M **10**-A; (c) 0.10 M (*S*)-**9b**-A, 0.10 M **10**-A.

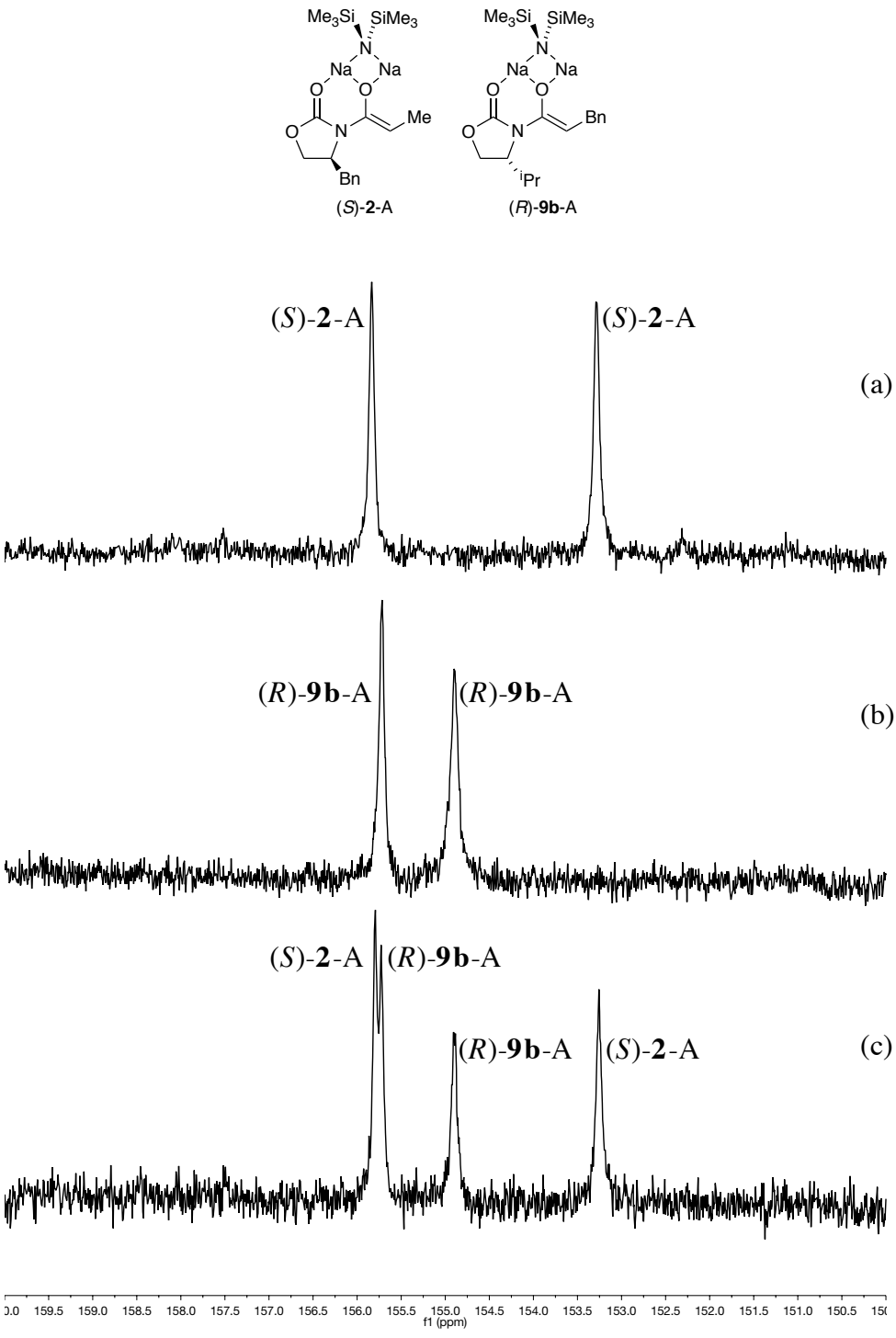


Figure A.2.28. ^{13}C NMR spectra in 1.0 M (*S,S*)-TMCDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.20 M (*R*)-**9b**-A; (c) 0.10 M (*S*)-**2**-A, 0.10 M (*R*)-**9b**-A.

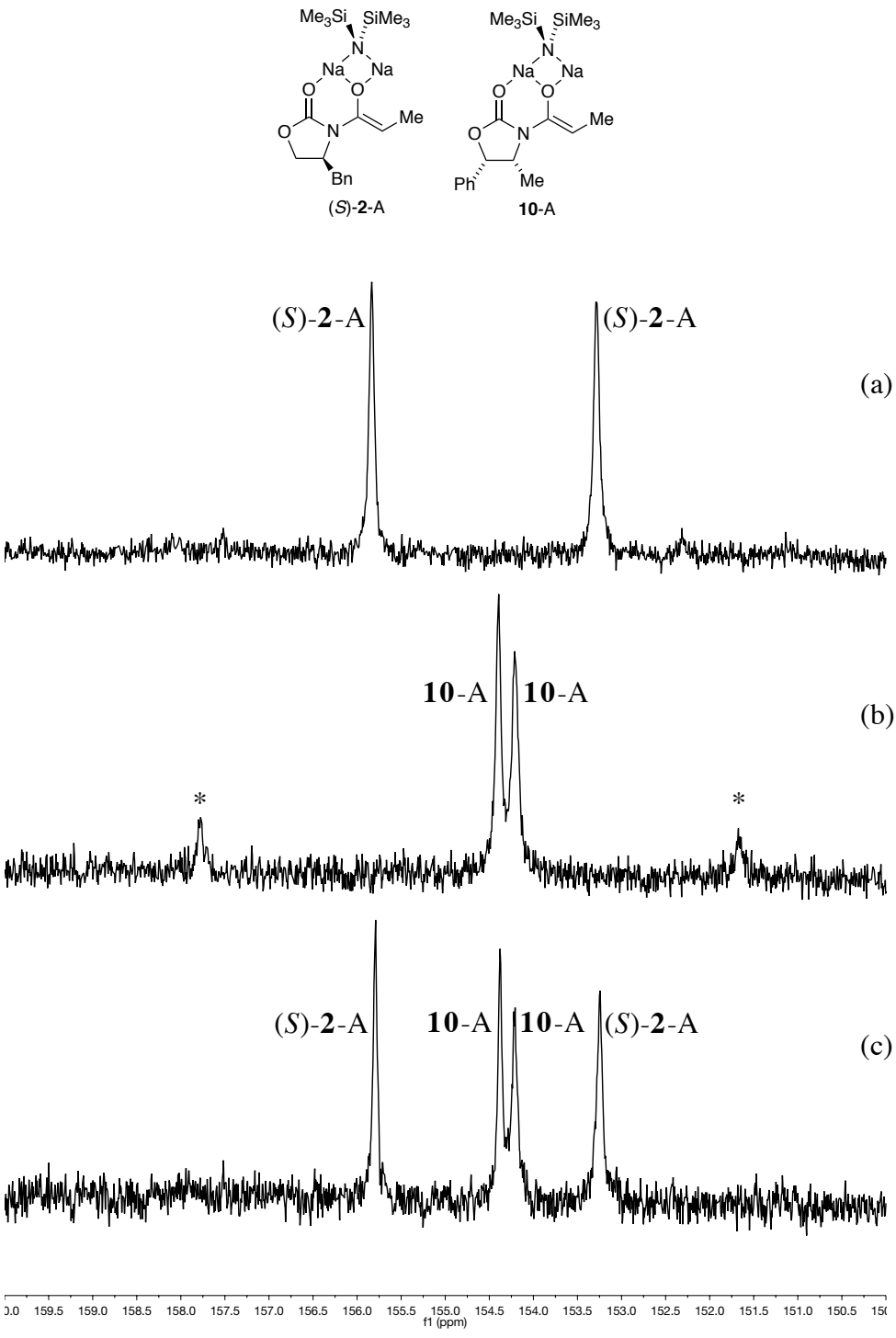


Figure A.2.29. ^{13}C NMR spectra in 1.0 M (*S,S*)-TMCDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.20 M **10**-A; (c) 0.10 M (*S*)-**2**-A, 0.10 M **10**-A.
* homoaggregate residue

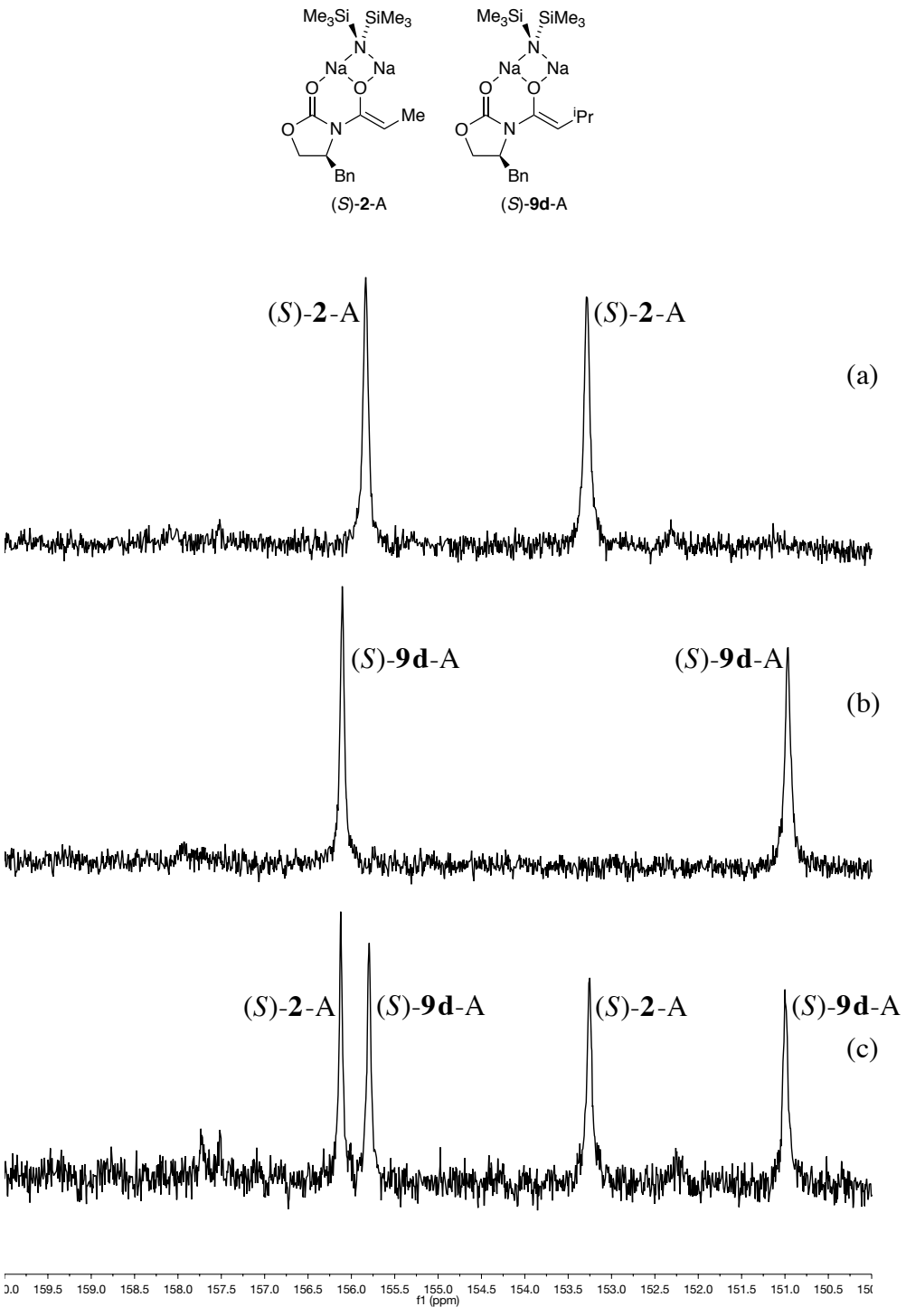


Figure A.2.30. ^{13}C NMR spectra in 1.0 M (*S,S*)-TMCDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**2**-A; (b) 0.20 M (*S*)-**9d**-A; (c) 0.10 M (*S*)-**2**-A, 0.10 M (*S*)-**9d**-A.

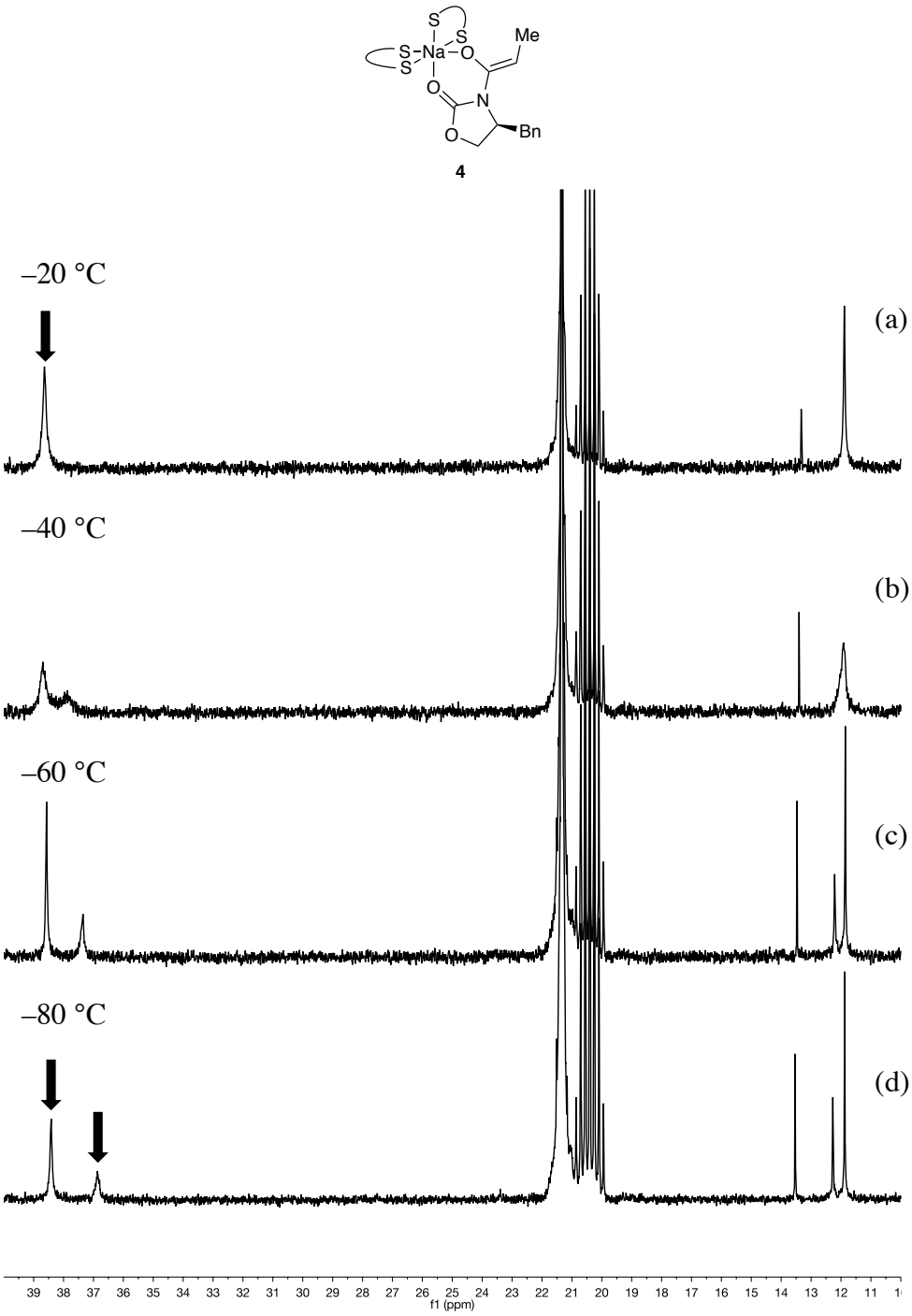


Figure A.2.31. ^{13}C NMR spectra of 0.20 M **4** and 0.10 M NaHMDS in 1.0 M TMEDA/toluene recorded at (a) –20 °C; (b) –40 °C; (c) –60 °C; (d) –80 °C. Gradually increasing the temperature of a tube consisting of shows coalescence at approximately –20 °C.

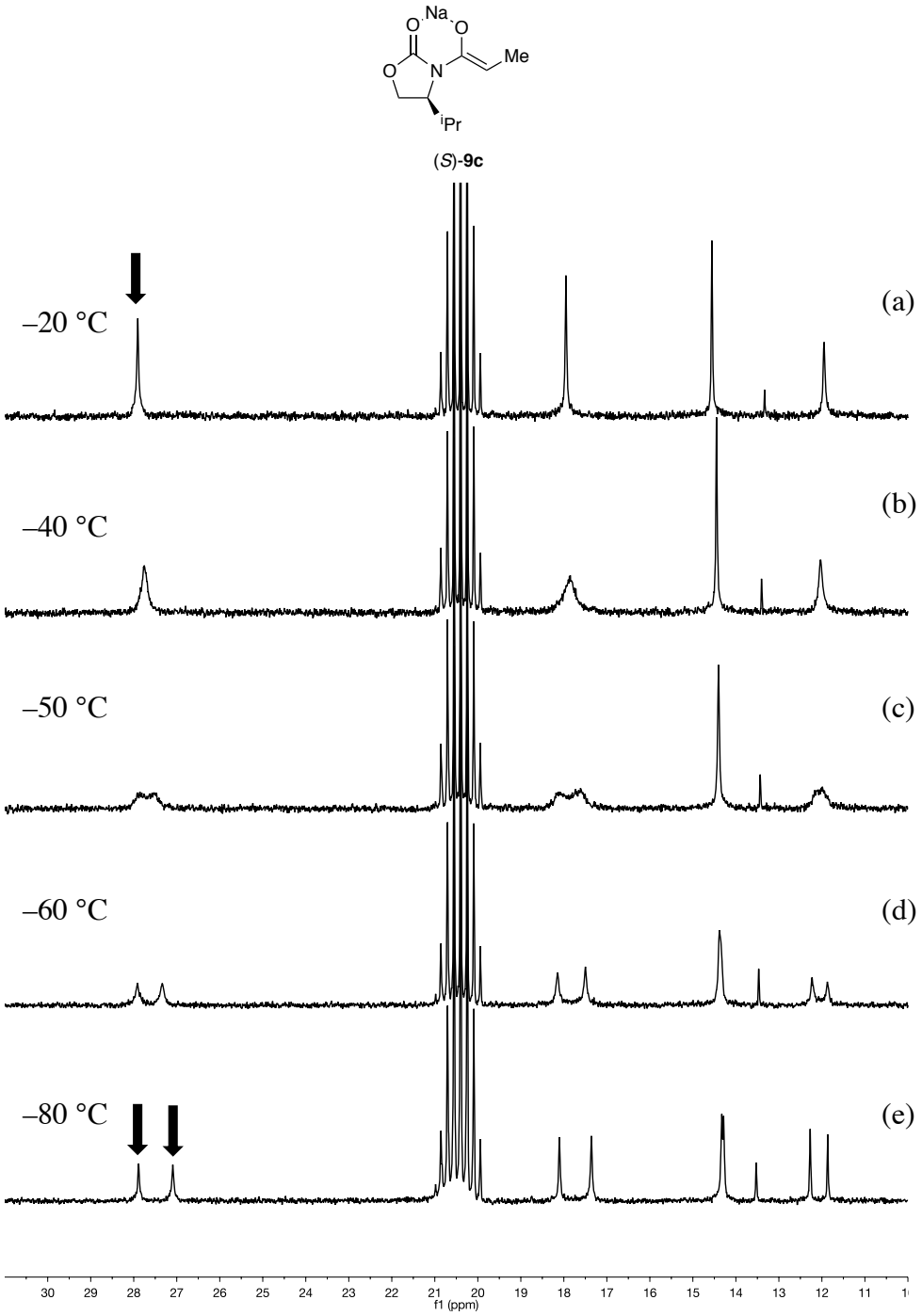


Figure A.2.32. ^{13}C NMR spectra of 0.20 M (*S*)-**9c** and 0.10 M NaHMDS in 1.0 M TMEDA/toluene recorded at (a) –20 °C; (b) –40 °C; (c) –50 °C; (d) –60 °C; (e) –80 °C.

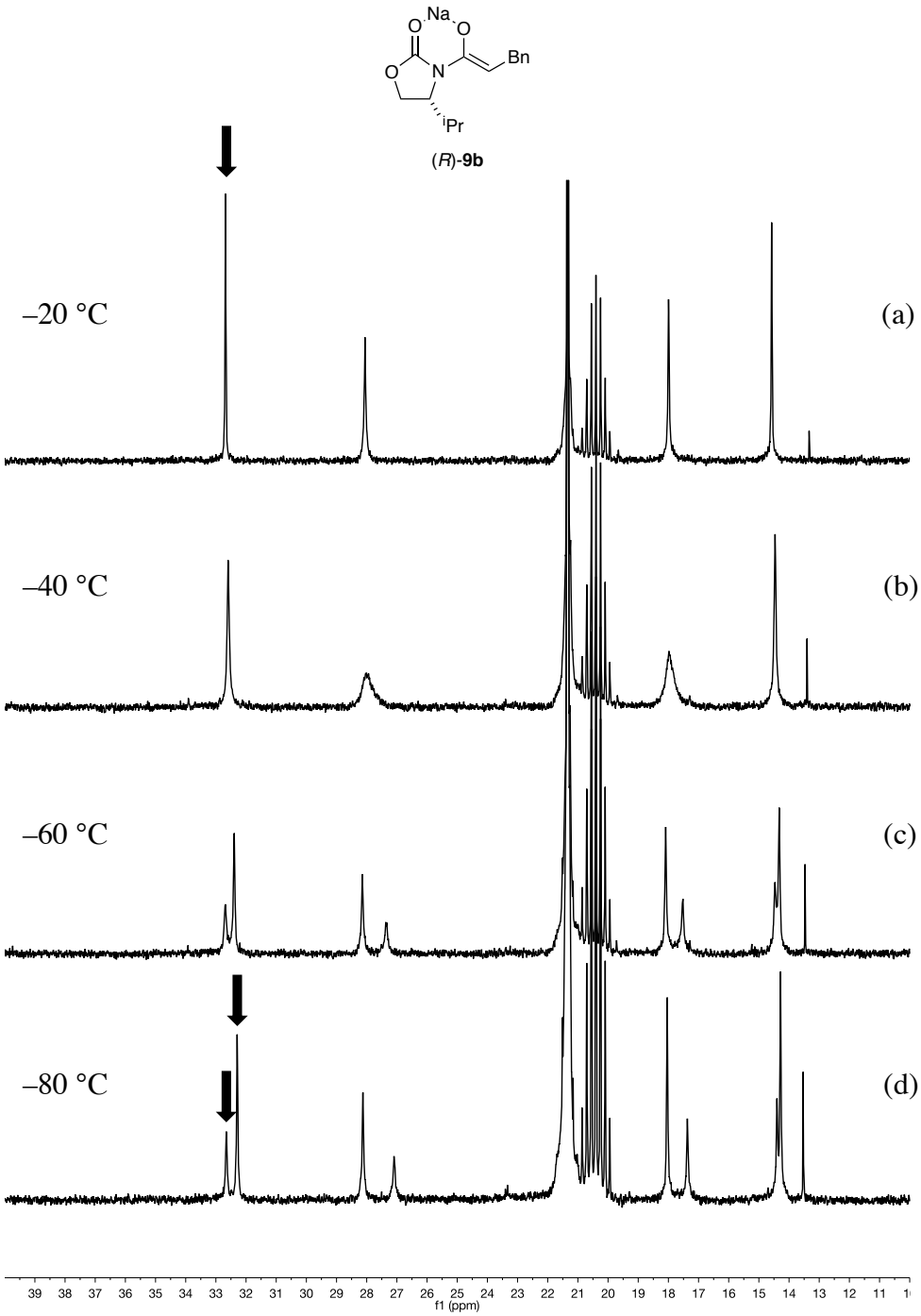


Figure A.2.33. ^{13}C NMR spectra of 0.20 M (*R*)-**9b** and 0.10 M NaHMDS in 1.0 M TMEDA/toluene recorded at (a) –20 °C; (b) –40 °C; (c) –60 °C; (d) –80 °C.

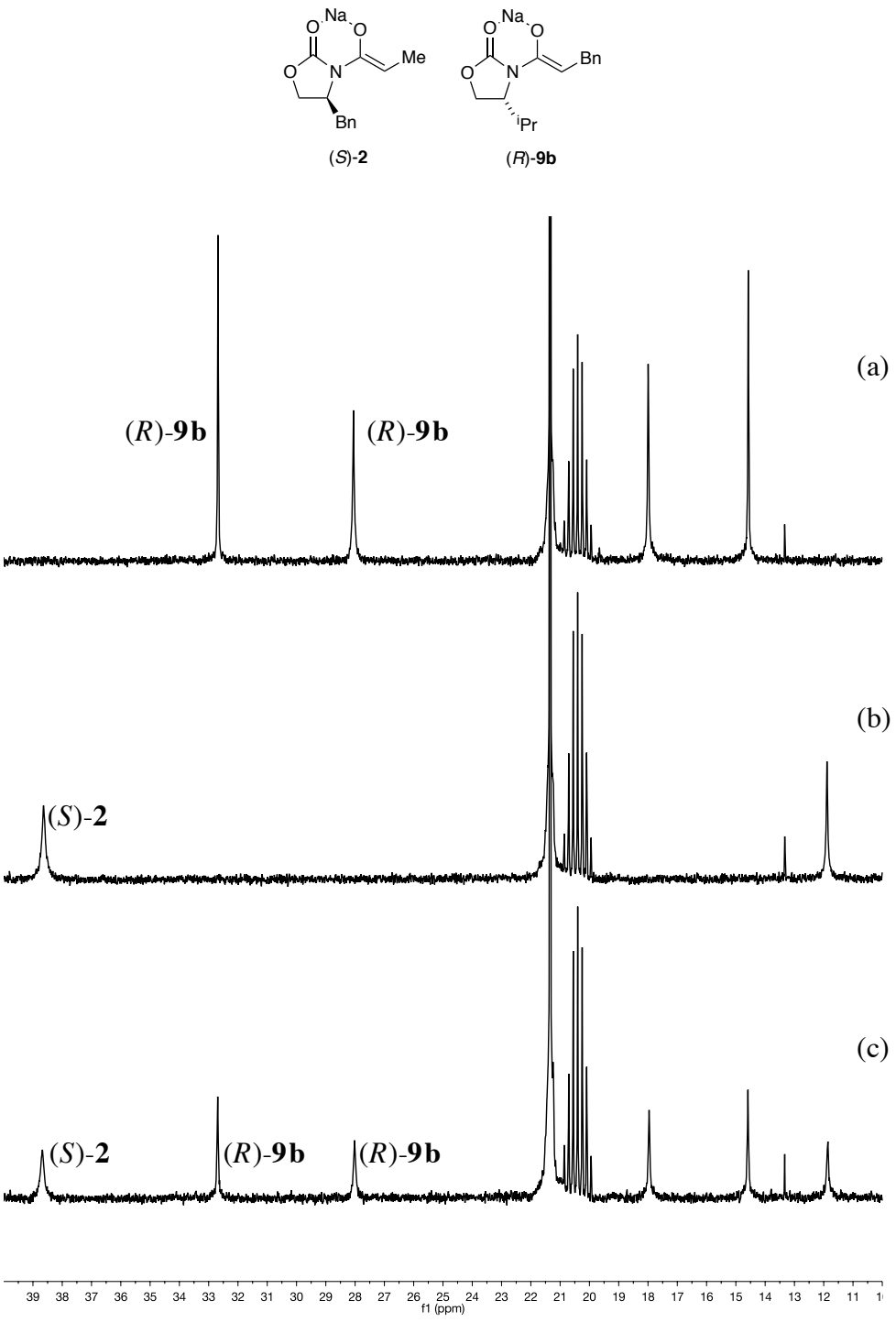


Figure A.2.34. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –20 °C of 0.10 M NaHMDS and (a) 0.20 M (*R*)-**9b**; (b) 0.20 M (*S*)-**2**; (c) 0.10 M (*R*)-**9b**, 0.10 M (*S*)-**2**. Mixing (*S*)-**2** and (*R*)-**9b** enolate at a temperature in which inter-aggregate exchange between monomer and NaHMDS mixed dimer is fast shows no chemical shift change.

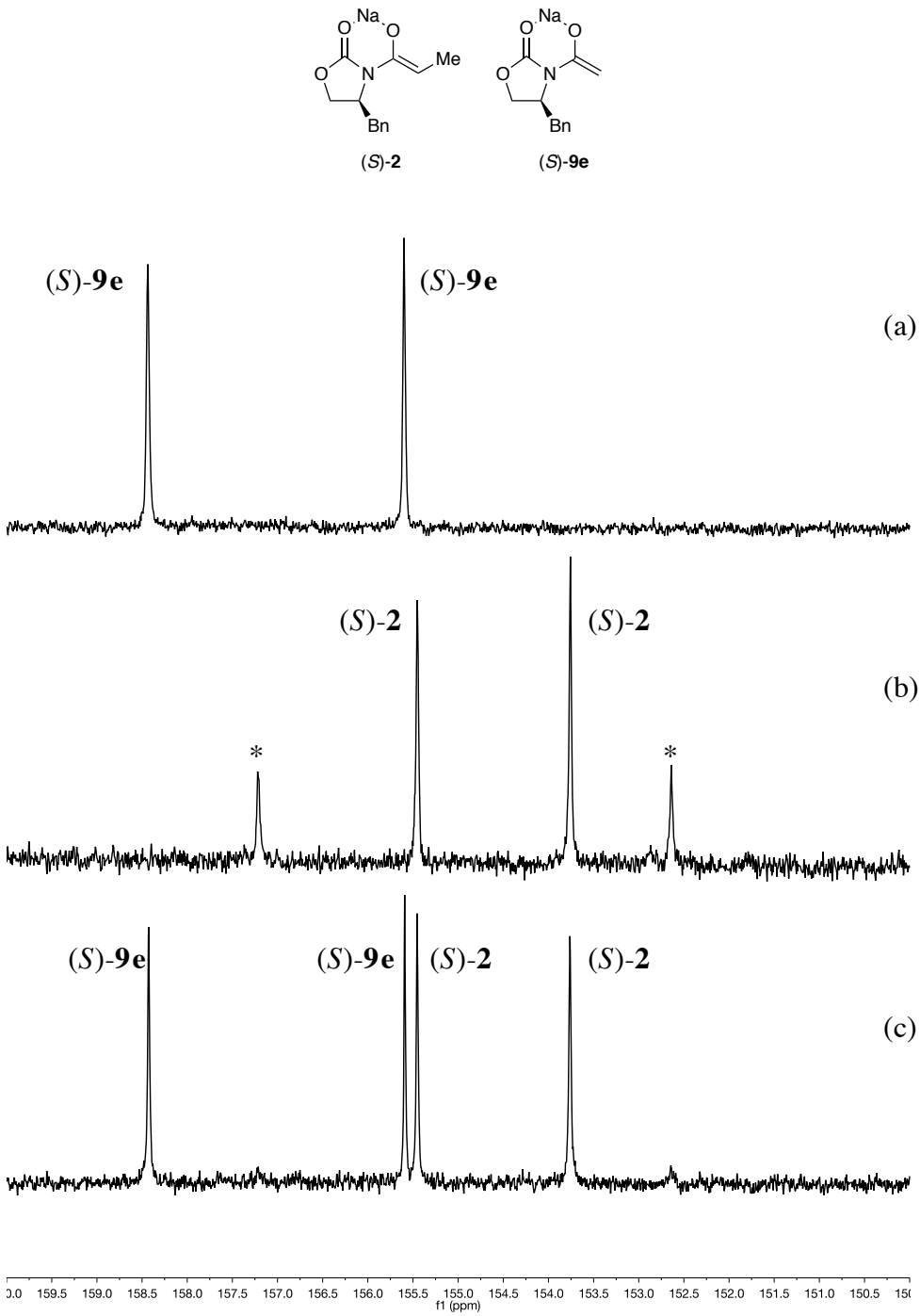


Figure A.2.35. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of 0.10 M NaHMDS and (a) 0.20 M (*S*)-**9e**; (b) 0.20 M (*S*)-**2**; (c) 0.10 M (*S*)-**9e**, 0.10 M (*S*)-**2**.
* homoaggregate residue

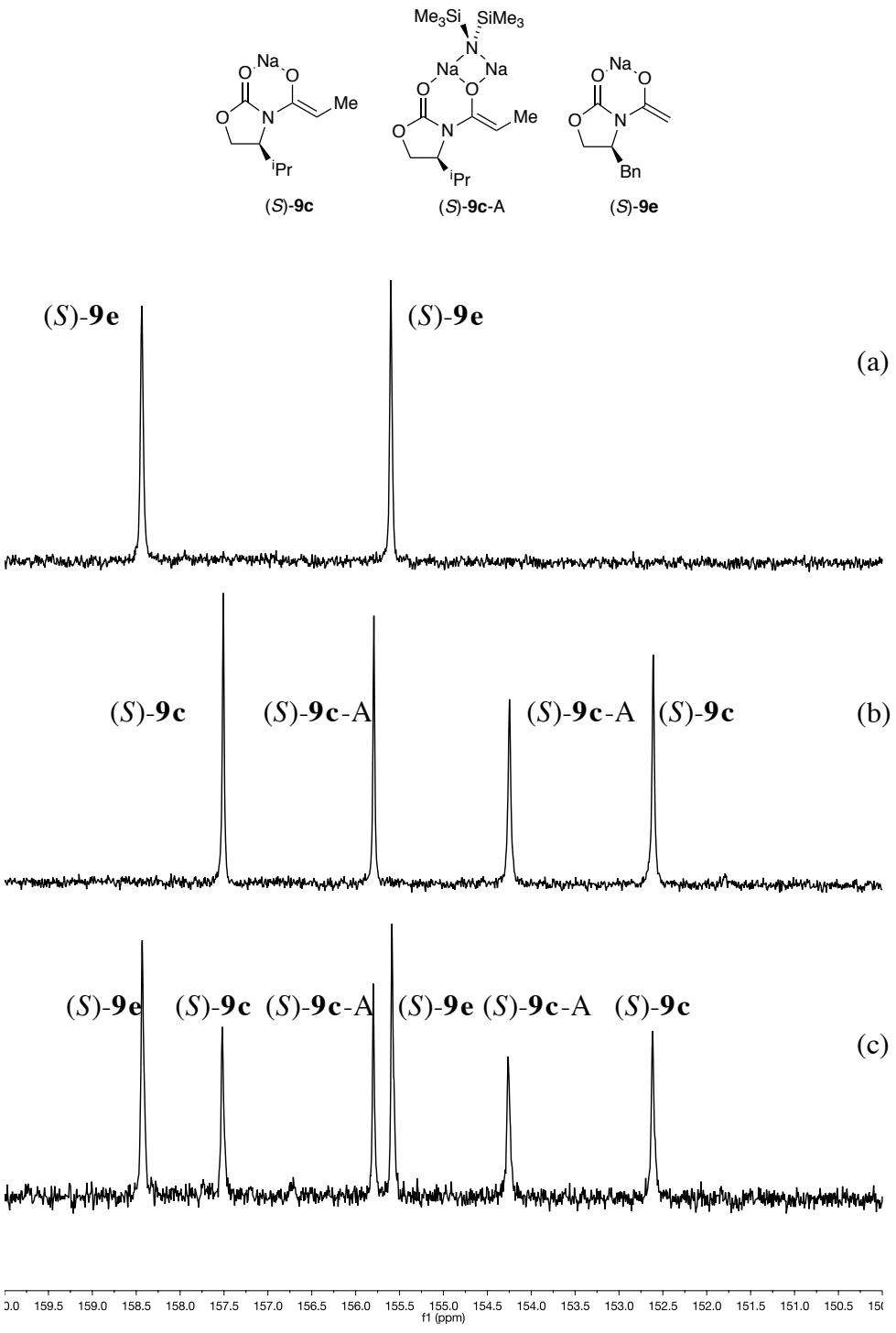


Figure A.2.36. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of 0.10 M NaHMDS and (a) 0.20 M (*S*)-**9e**; (b) 0.20 M (*S*)-**9c**; (c) 0.10 M (*S*)-**9e**, 0.10 M (*S*)-**9c**.

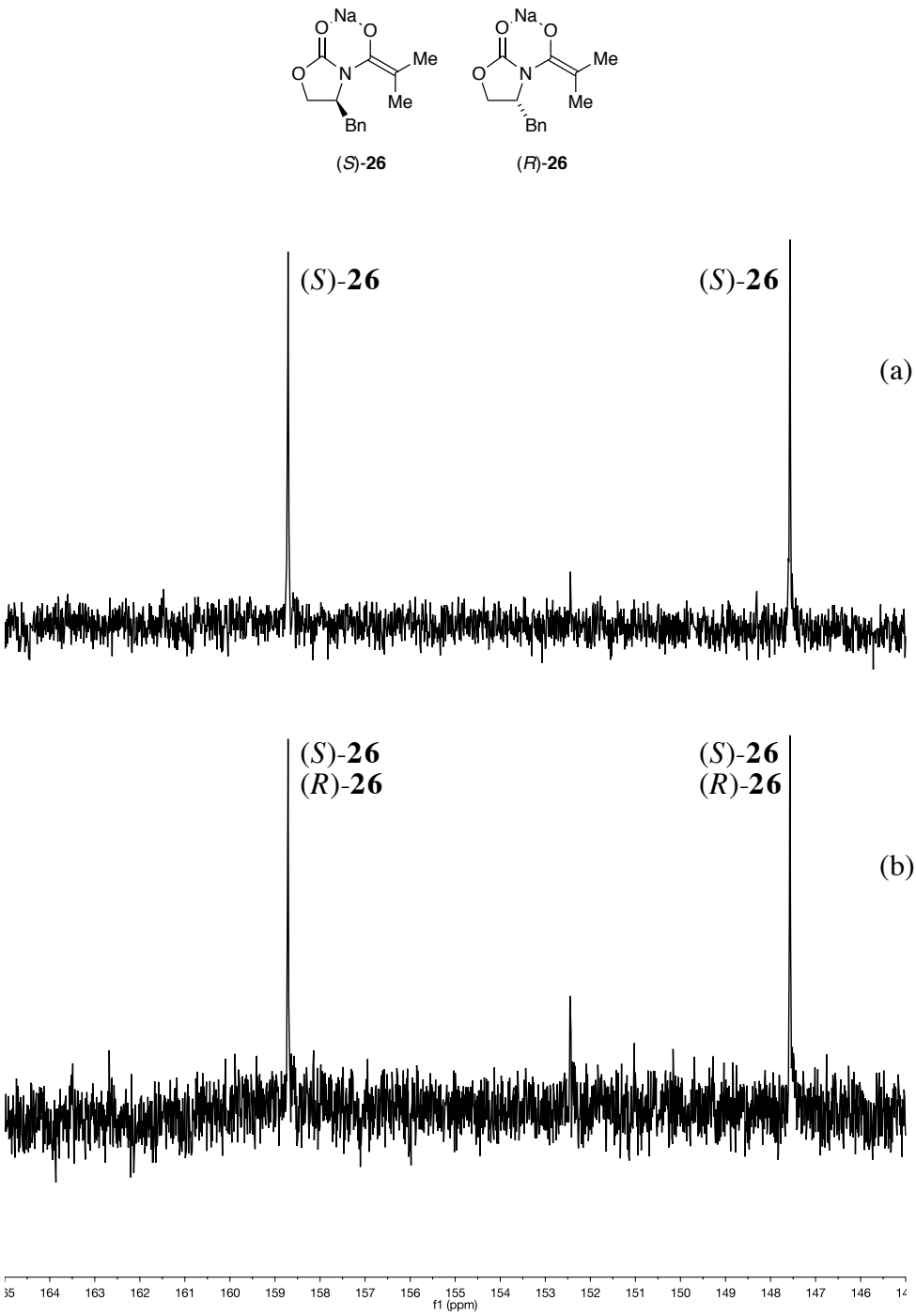


Figure A.2.37. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M (*S*)-**26**; (b) 0.10 M (*S*)-**26**, 0.10 M (*R*)-**26**.
The tube was aged at 0 °C for 10 minutes to complete the enolization of (*S*)-**26**, leading to some decomposition.

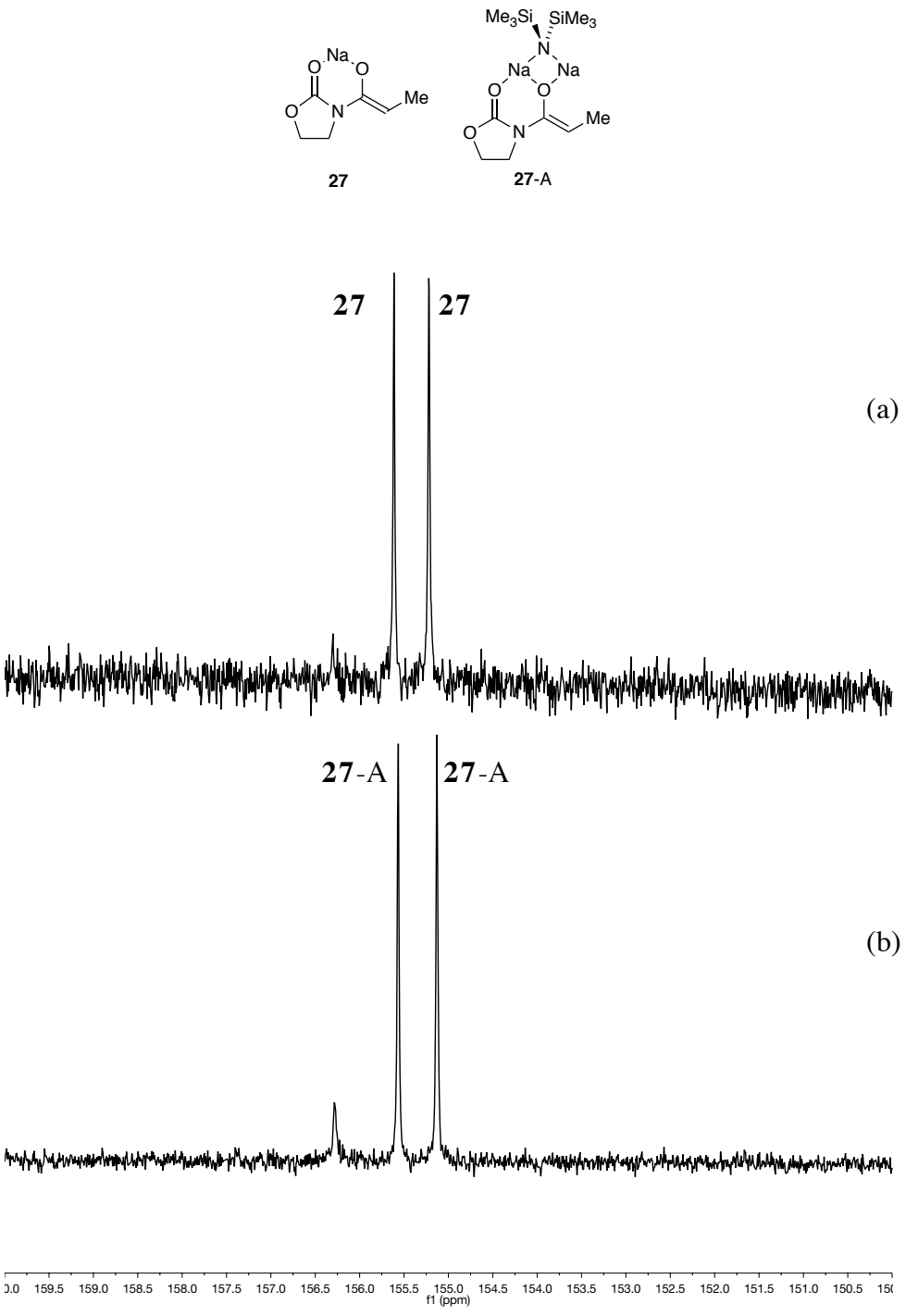


Figure A.2.38. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M **27**; (b) 0.20 M **27**-A.

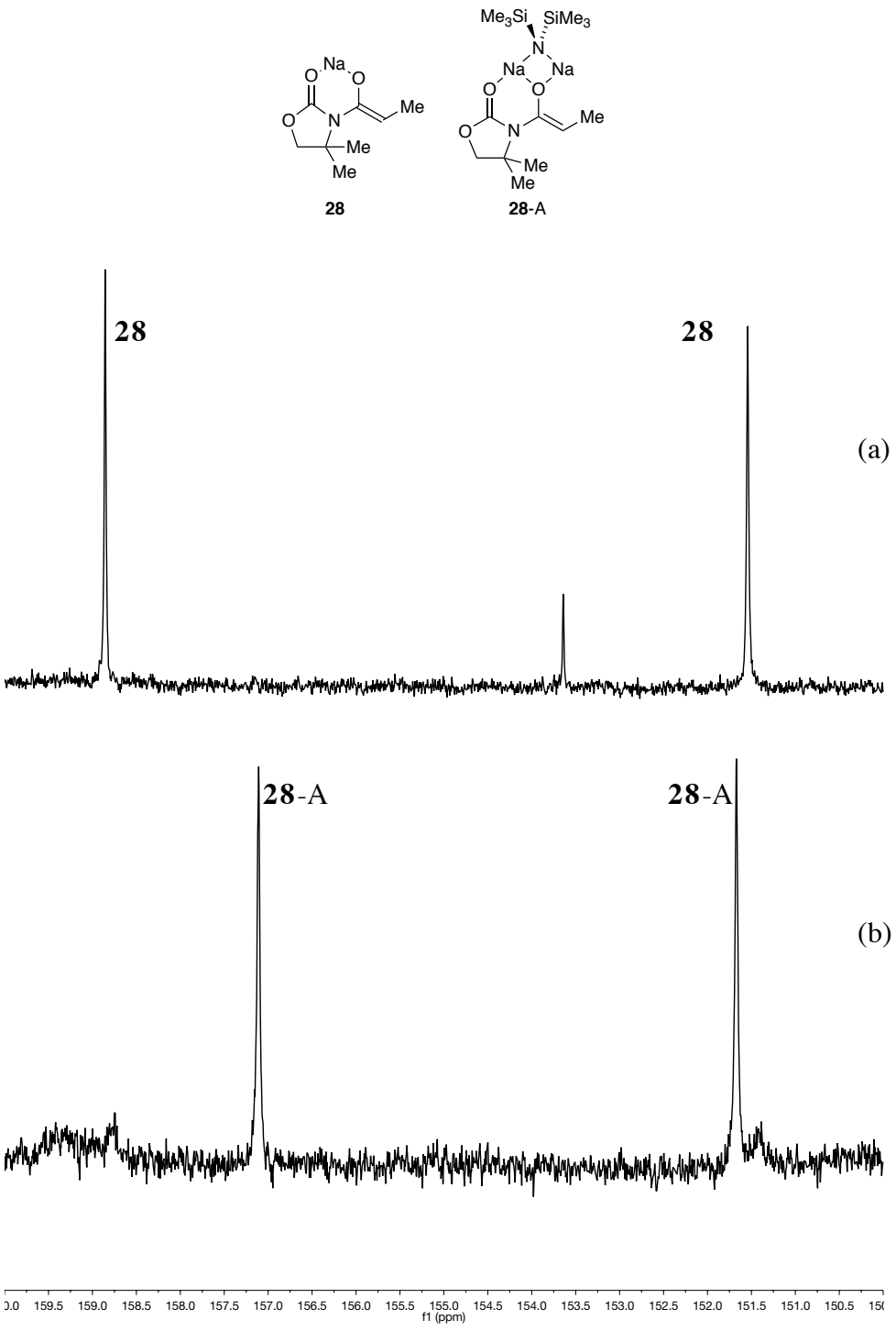


Figure A.2.39. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M **28**; (b) 0.20 M **28**-A.

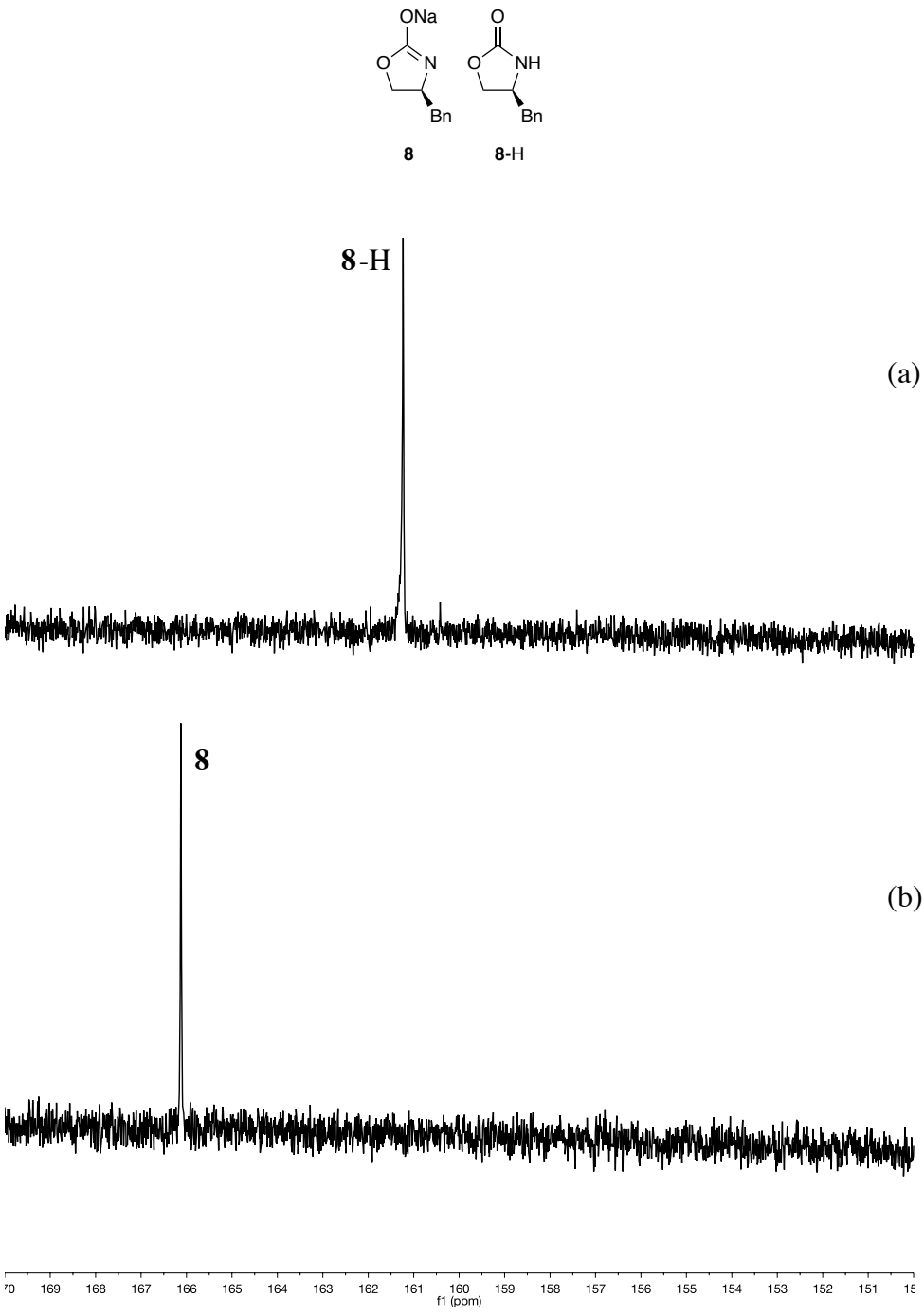


Figure A.2.40. ^{13}C NMR spectra in 1.0 M TMEDA/toluene recorded at –80 °C of (a) 0.20 M **8**-H; (b) 0.20 M **8**. Enolate **8** often precipitates out of solution.

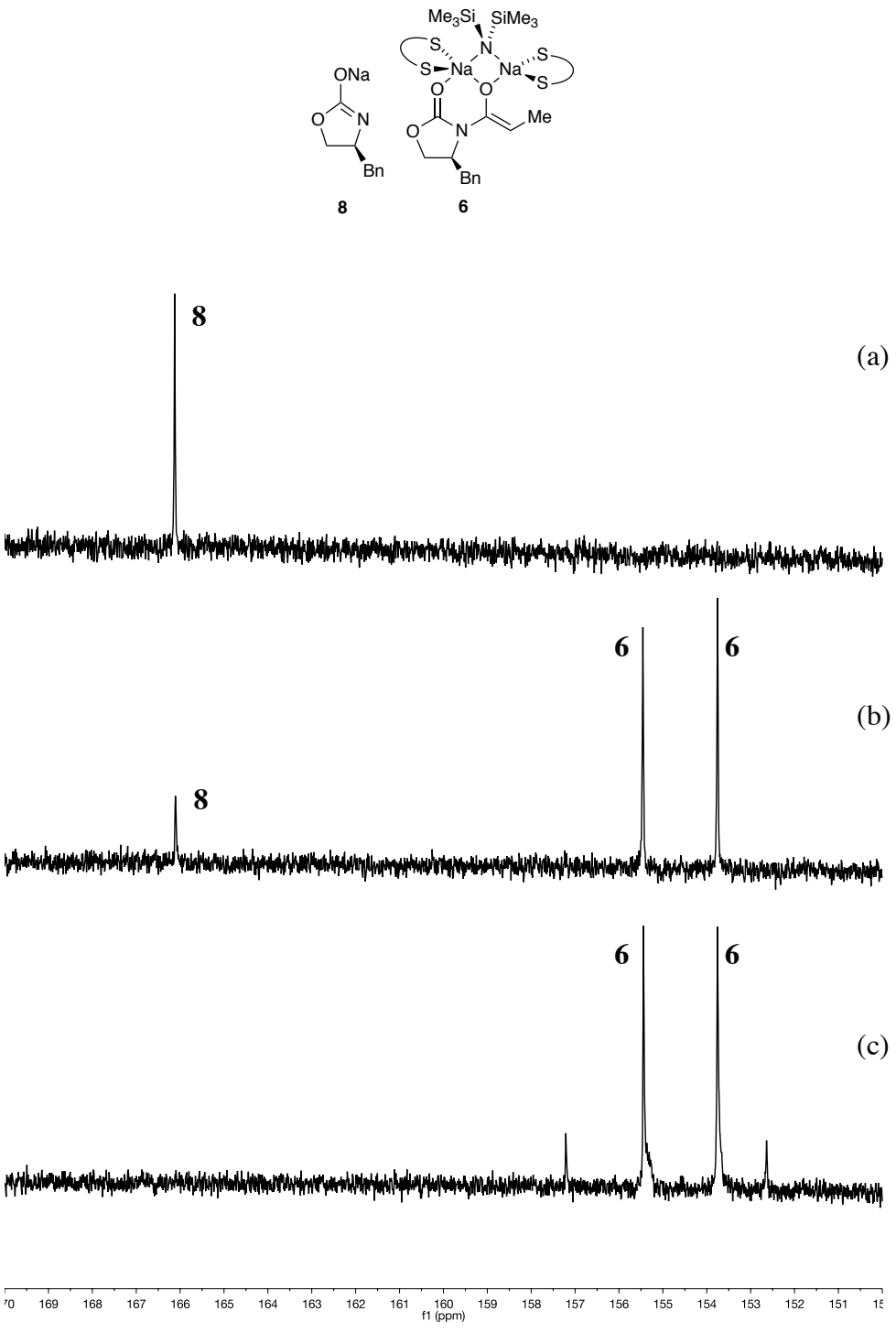


Figure A.2.41. ^{13}C NMR spectra of (a) 0.20 M **8**; (b) 0.10 M **8** and 0.10 M **6**; (c) 0.20 M **6** and 0.10 M NaHMDS in 1.0 M TMEDA in toluene recorded at –80 °C. No evidence of mixed aggregates are observable.

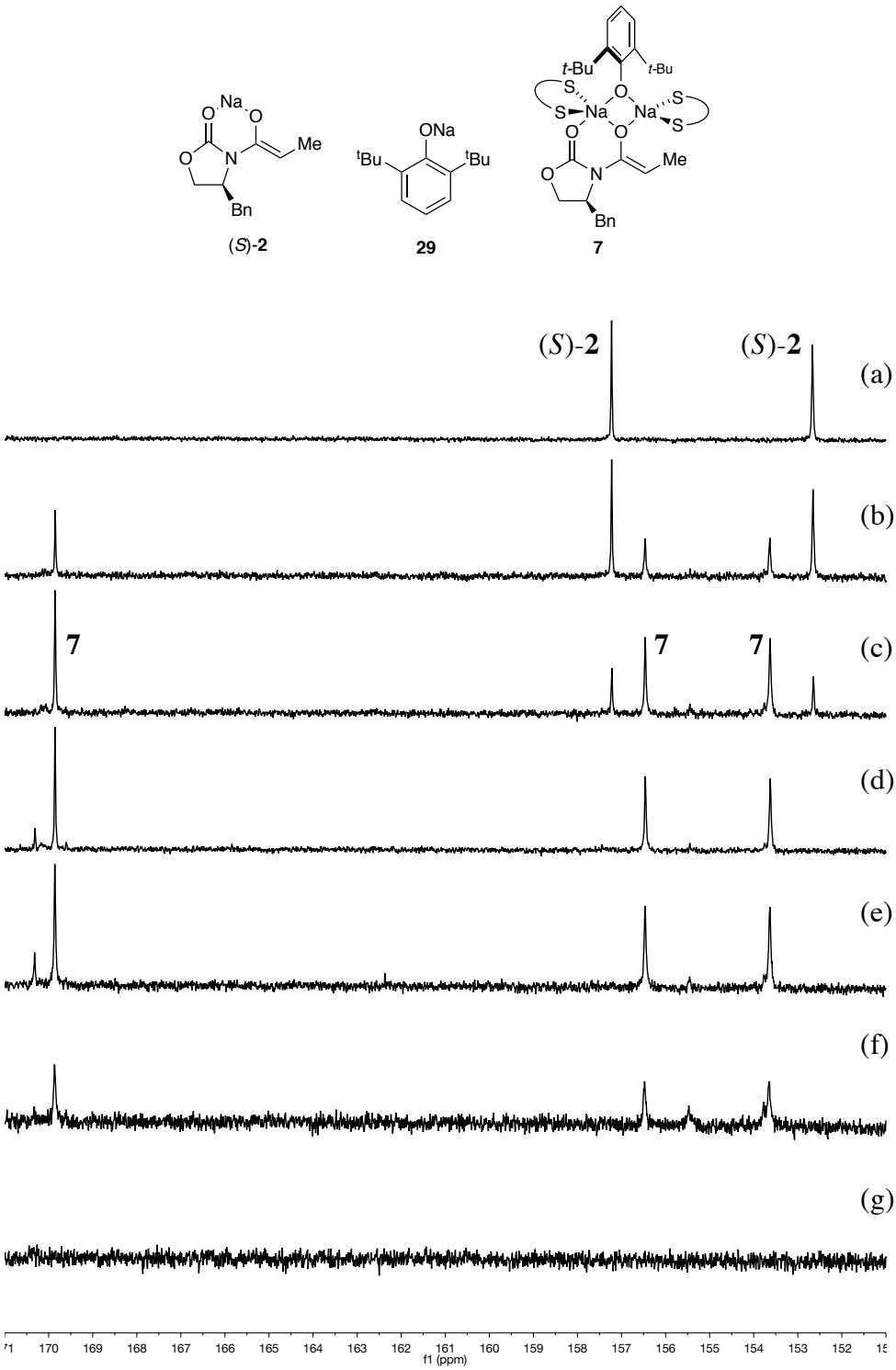


Figure A.2.42. ^{13}C NMR spectra of (a) 0.30 M (*S*)-**2**; (b) 0.25 M (*S*)-**2** and 0.05 M **29**; (c) 0.20 M (*S*)-**2** and 0.10 M **29**; (d) 0.15 M (*S*)-**2** and 0.15 M **29**; (e) 0.10 M (*S*)-**2** and 0.20 M **29**; (f) 0.05 M (*S*)-**2** and 0.25 M **29**; (g) 0.30 M **29** in 1.0 M TMEDA in toluene recorded at –80 °C. Phenolate **29** forms a mixed dimer with (*S*)-**2** quantitatively. Phenolate **29** is insoluble in the absence of (*S*)-**2**. .

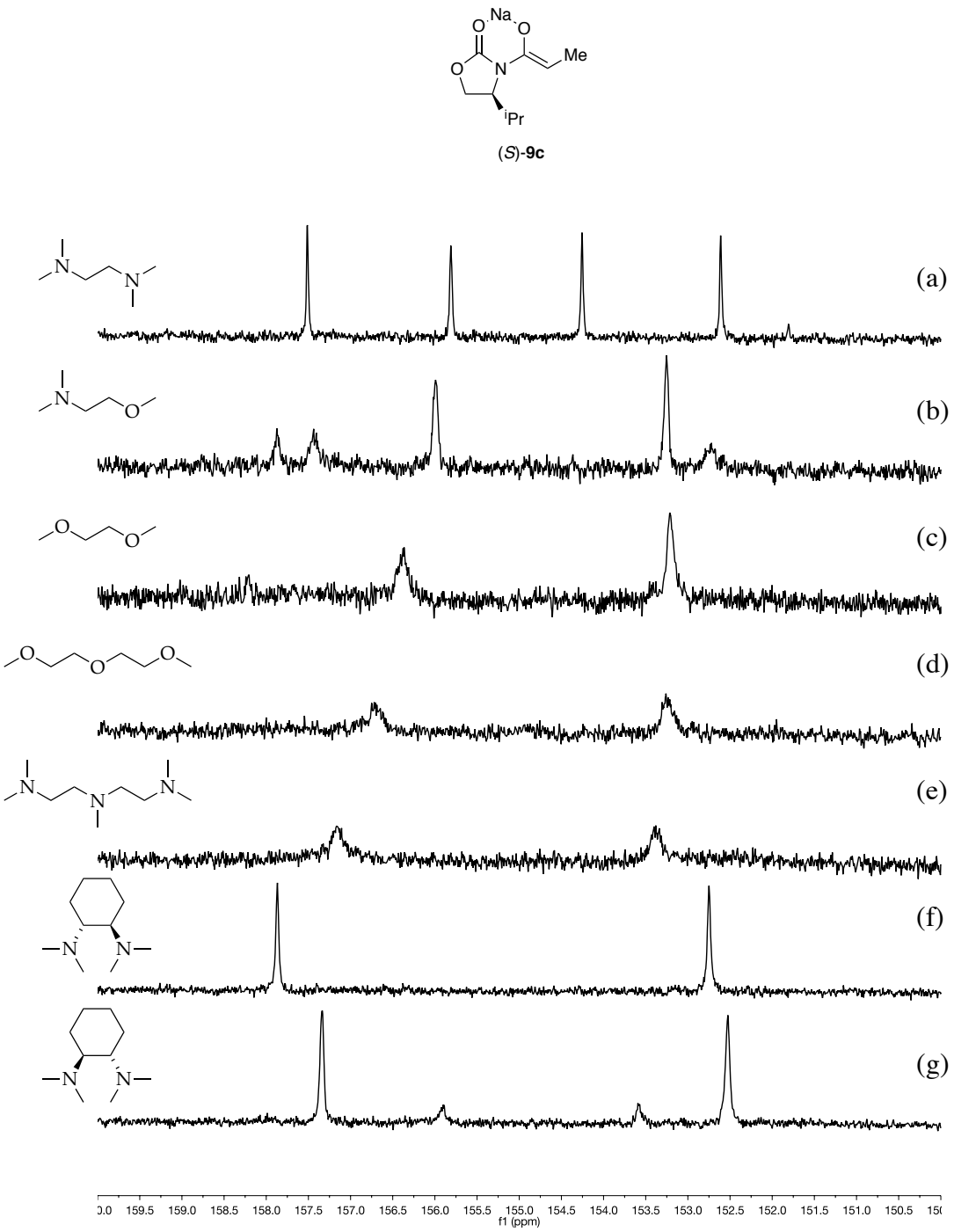


Figure A.2.43. ^{13}C NMR spectra of 0.20 M (*S*)-**9c** and 0.10 M NaHMDS in 1.0 M (a) TMEDA; (b) *N,N*-dimethyl-2-methoxyethylamine; (c) DME; (d) diglyme; (e) PMDTA; (f) (*R*,*R*)-TMCDA; (g) (*S*,*S*)-TMCDA in toluene recorded at –80 °C.

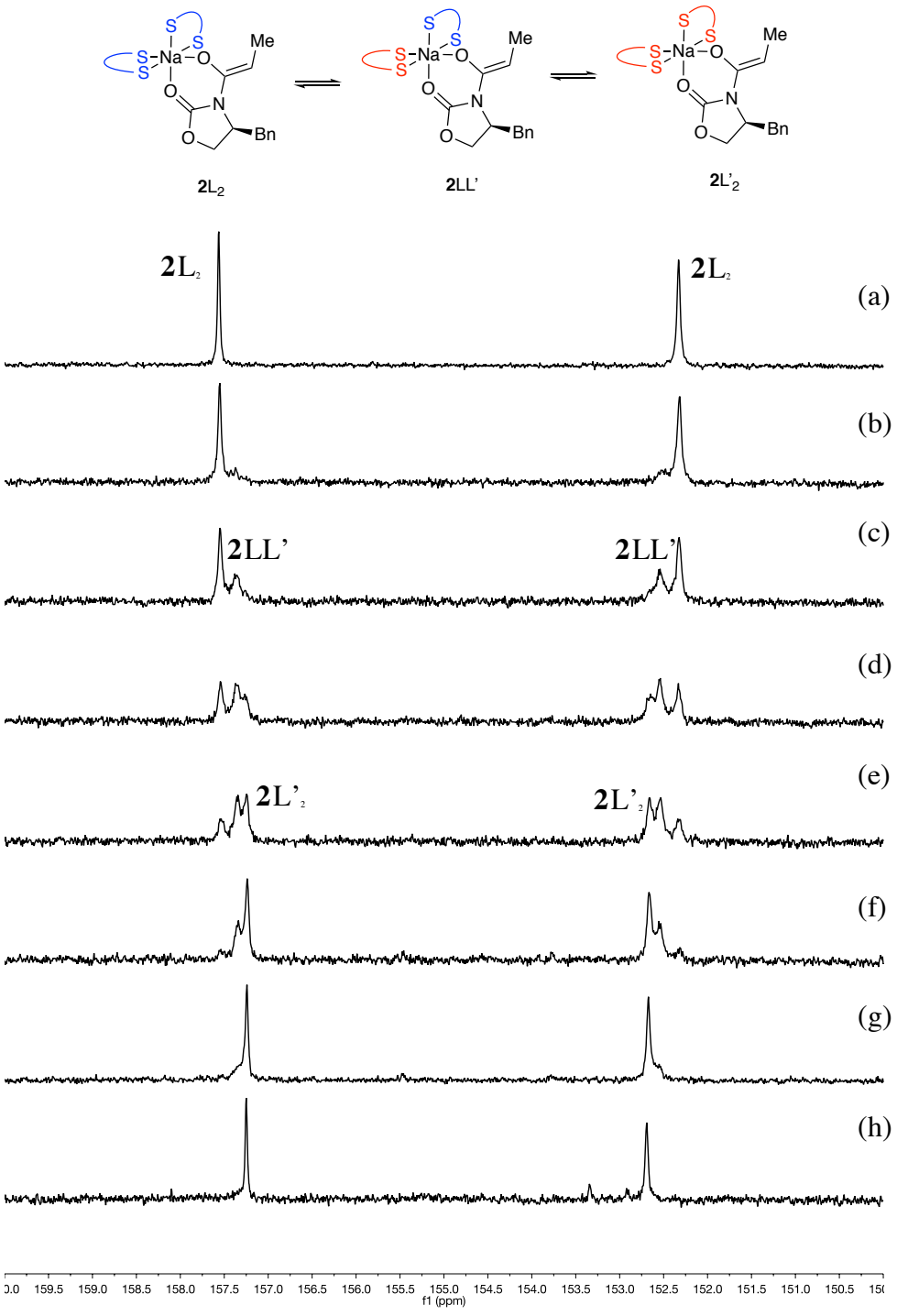
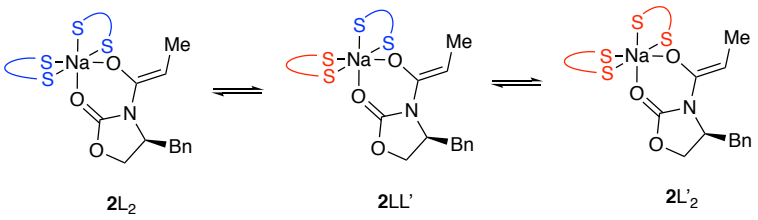


Figure A.2.44. ^{13}C NMR spectra of 0.20 M **4** and TMEDA and (*S*,*S*)-TMCDA (1.0 total ligand titer) in toluene recorded at –80 °C. The intended mole fractions for (*S*,*S*)-TMCDA, X_B, in (a)–(h) are 0.00, 0.10, 0.20, 0.30, 0.40, 0.60, 0.80 and 1.00, respectively. L = TMEDA; L' = (*S*,*S*)-TMCDA. The experiment shows that monomer **4** forms a mixed solvate species, confirming the solvation number of the homosolvates.



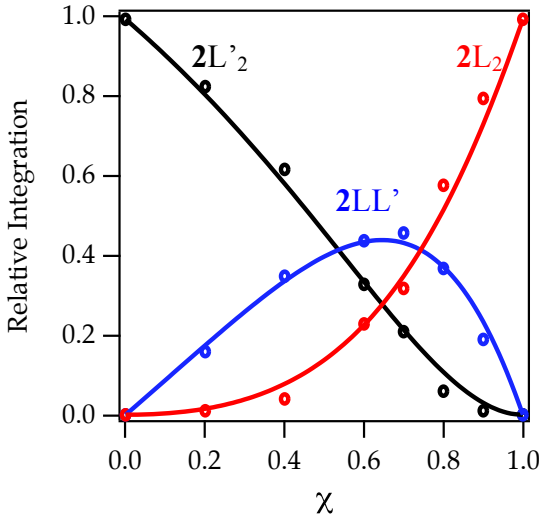
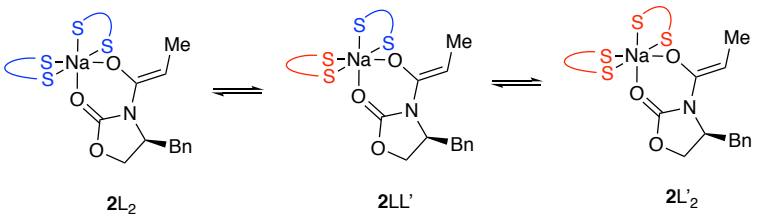


Figure A.2.45. Job plot showing the relative integrations versus the intended mole fraction of TMEDA for 0.20 M **4** and 1.0 M total TMEDA and (*S*,*S*)-TMCDA in toluene recorded at −80 °C. The curves represent a parametric fit to a dimer model that includes provisions for relative binding affinities to the disolvated monomer. The 'shift' of the maximum for the mixed solvate from 0.50 results from the differential binding constants. L = TMEDA; L' = (*S*,*S*)-TMCDA.



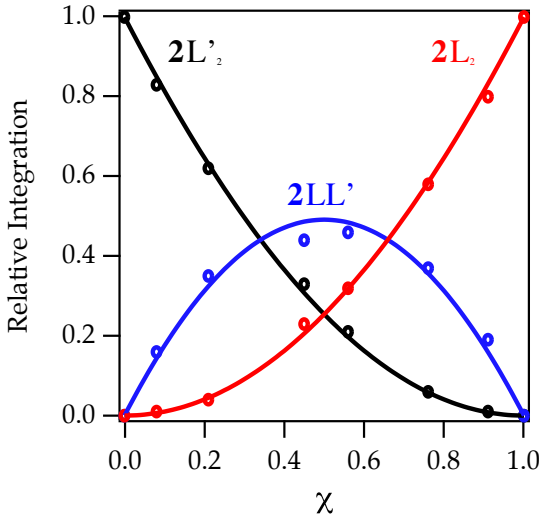


Figure A.2.46. Job plot showing the relative integrations versus the *measured* mole fraction of TMEDA for 0.20 M **4** with added TMEDA and (*S*,*S*)-TMCDA (1.0 M total ligand titer) in toluene recorded at −80 °C. L = TMEDA; L' = (*S*,*S*)-TMCDA.

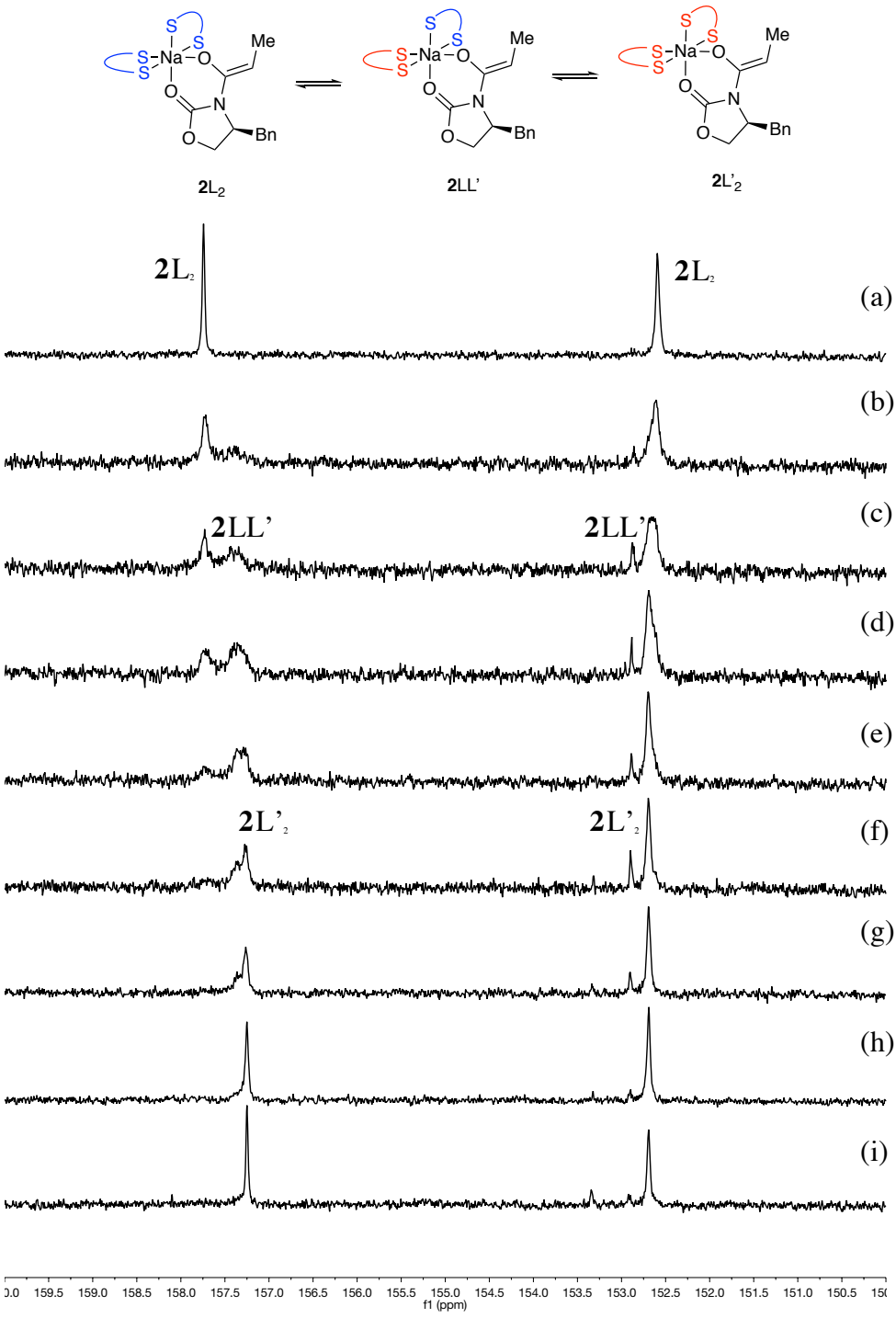
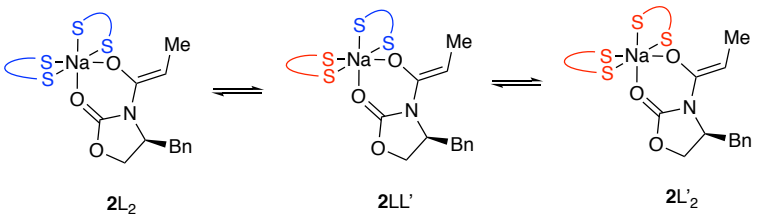


Figure A.2.47. ^{13}C NMR spectra of 0.20 M **4** with TMEDA and (*R*,*R*)-TMCDA (1.0 M total ligand titer) in toluene recorded at –80 °C. The intended mole fractions for (*R*,*R*)-TMCDA, X_B, in (a)–(i) are 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80 and 1.00, respectively. L = TMEDA, L' = (*R*,*R*)-TMCDA.



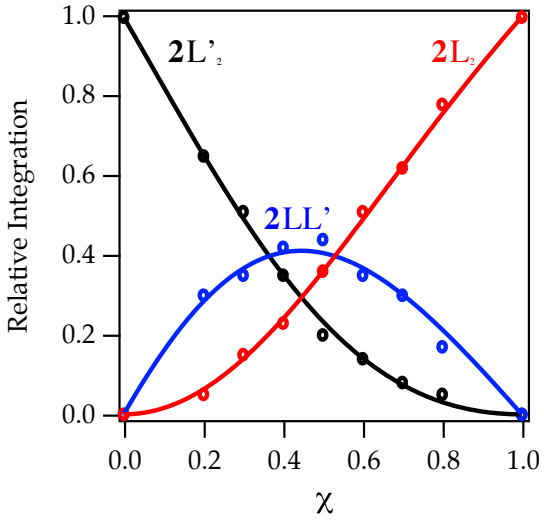
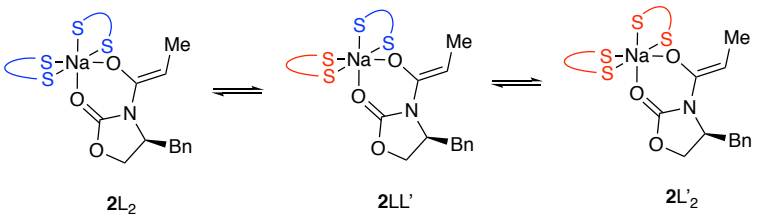


Figure A.2.48. Job plot showing the relative integrations versus the intended mole fraction of TMEDA for 0.20 M **4** and 1.0 M total TMEDA and (*R*,*R*)-TMCDA in toluene recorded at −80 °C. L = TMEDA, L' = (*R*,*R*)-TMCDA.



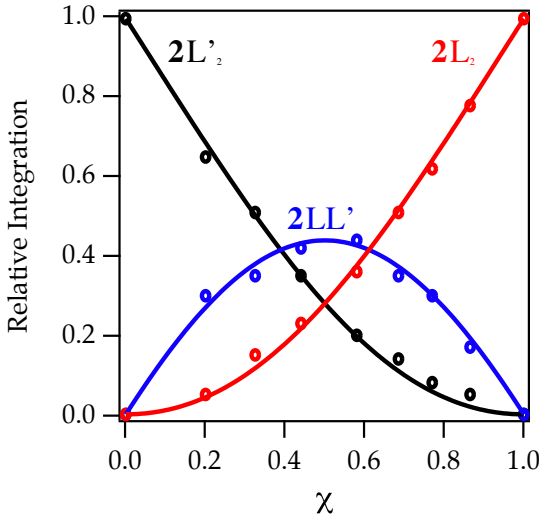


Figure A.2.49. Job plot showing the relative integrations versus the measured mole fraction of TMEDA for 0.20 M **4** and 1.0 M total TMEDA and (*R*,*R*)-TMCDA in toluene recorded at −80 °C.

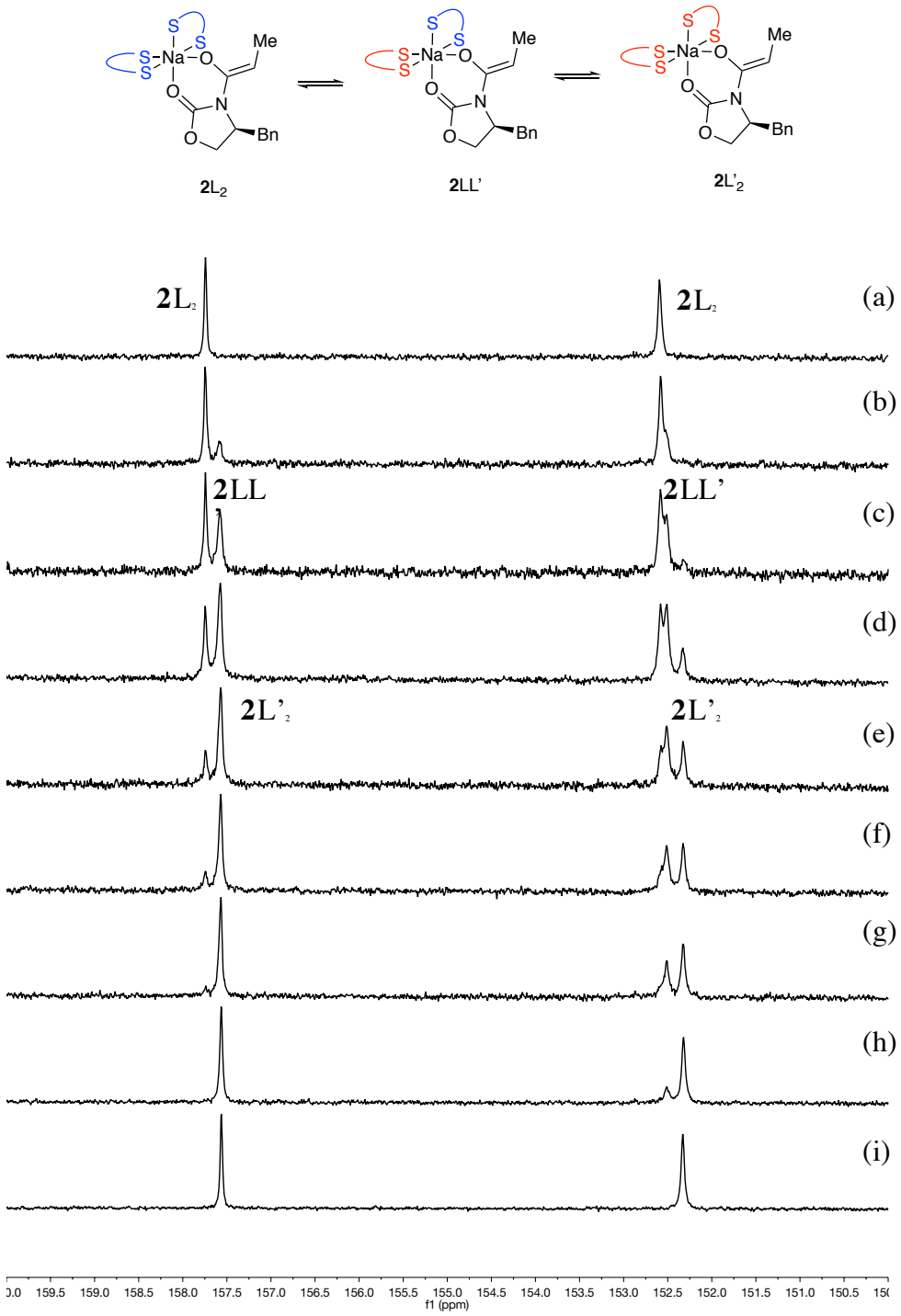
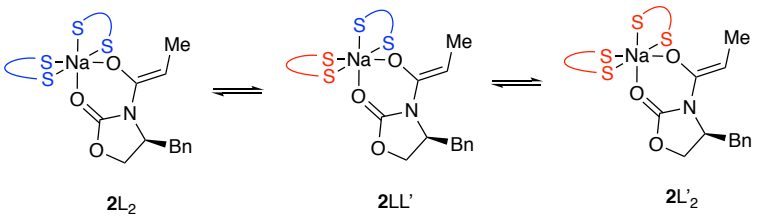


Figure A.2.50. ^{13}C NMR spectra of 0.20 M **4** in (*S*,*S*)-TMCDA and (*R*,*R*)-TMCDA mixtures (1.0 M total ligand titer) in toluene recorded at –80 °C. The intended mole fractions for (*R*,*R*)-TMCDA, X_B, in (a)–(i) are 0.00, 0.20, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90 and 1.00, respectively. L = (*S*,*S*)-TMCDA, L' = (*R*,*R*)-TMCDA.



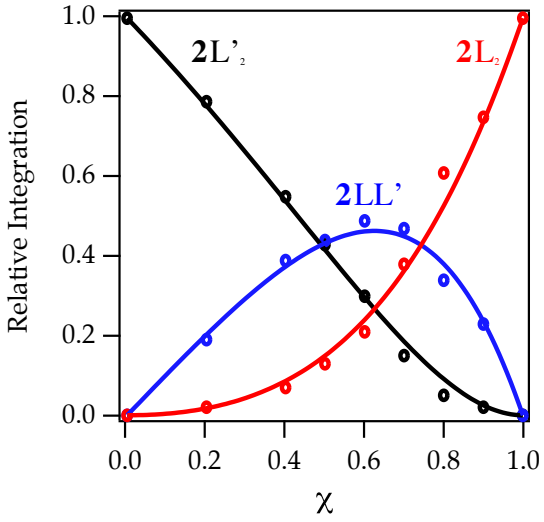
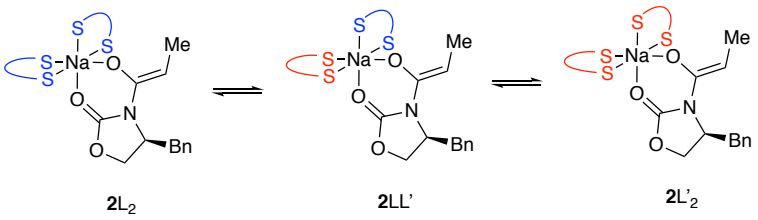


Figure A.2.51. Job plot showing the relative integrations versus the intended mole fraction of (*R*,*R*)-TMCDA for 0.20 M (*S*)-**2** in (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA mixtures (1.0 M total ligand titer) in toluene recorded at −80 °C. L = (*S*,*S*)-TMCDA, L' = (*R*,*R*)-TMCDA. The offset of the maximum to the right shows a relative preference for binding (*S*,*S*)-TMCDA versus (*R*,*R*)-TMCDA.



2L_2 **2**LL' **2**L'$_2$

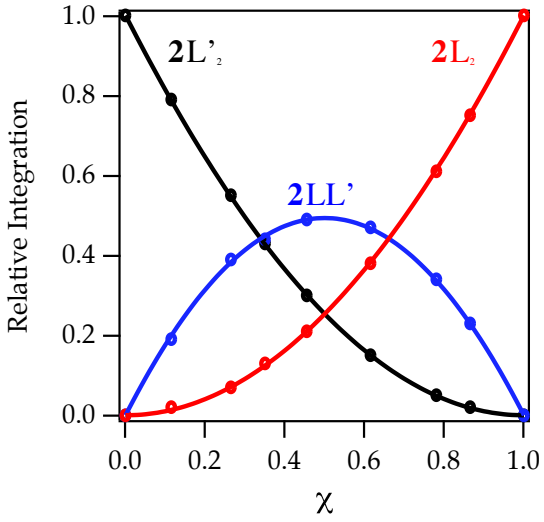


Figure A.2.52. Job plot showing the relative integrations versus the measured mole fraction of (*R*,*R*)-TMCDA for 0.20 M (*S*)-**2** and 1.0 M total (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA in toluene recorded at −80 °C. L = (*S*,*S*)-TMCDA, L' = (*R*,*R*)-TMCDA.

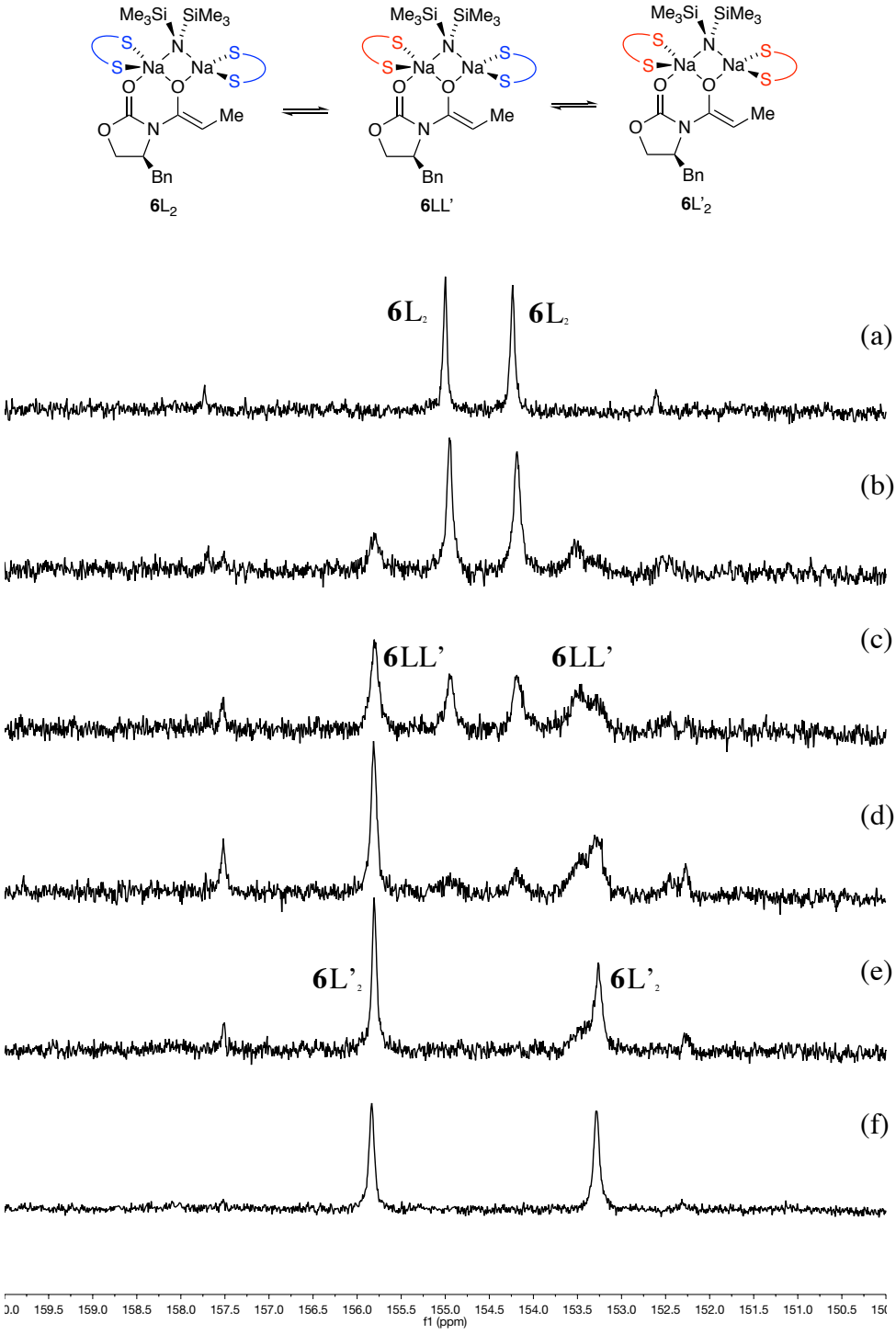


Figure A.2.53. ^{13}C NMR spectra of 0.20 M **6** and 1.0 M (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA in toluene recorded at –80 °C. The intended mole fractions for (*S*,*S*)-TMCDA, X_B, in (a)–(f) are 0.00, 0.20, 0.40, 0.60, 0.80, and 1.00, respectively. L = (*R*,*R*)-TMCDA, L' = (*S*,*S*)-TMCDA. The experiment shows two coordinated diamines.

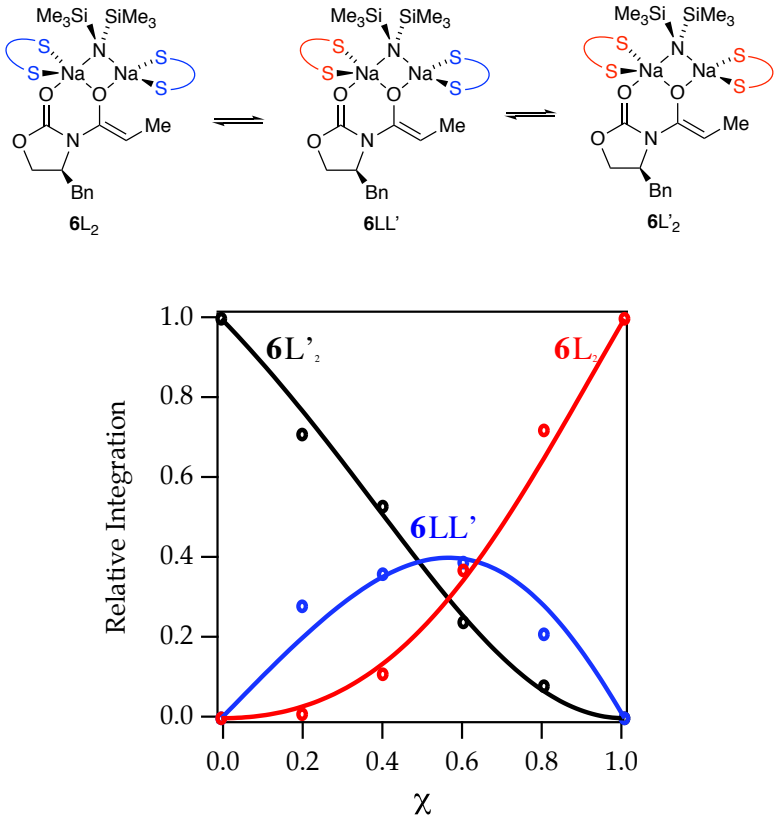


Figure A.2.54. Job plot showing the relative integrations versus the intended mole fraction of (*R*,*R*)-TMCDA for 0.20 M **6** and 1.0 M total (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA in toluene recorded at −80 °C. L = (*R*,*R*)-TMCDA, L' = (*S*,*S*)-TMCDA. Job plot indicates a disolvated dimer and shows minor differences in relative binding constants.

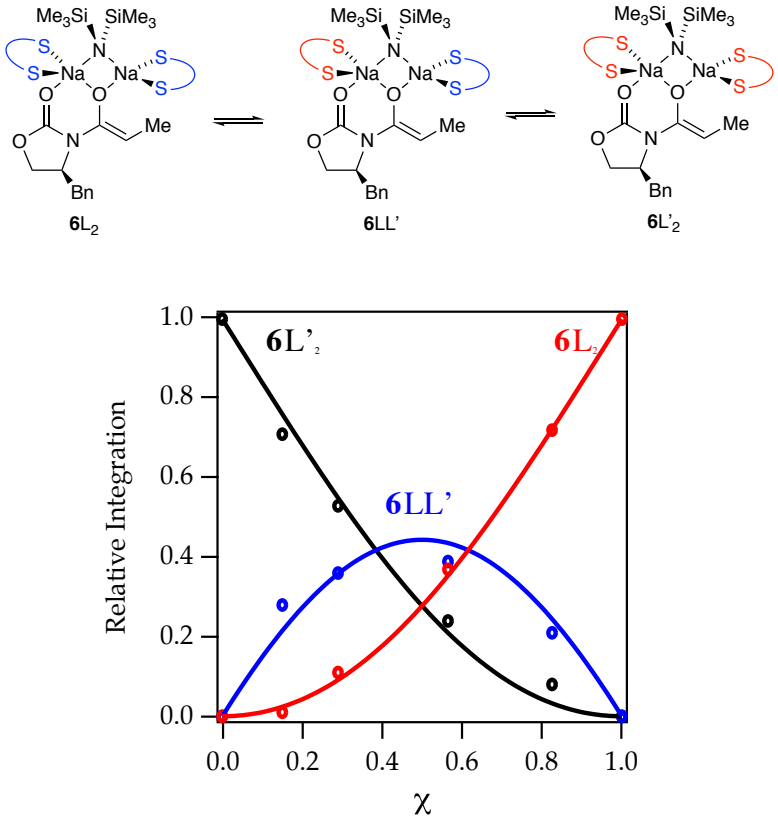


Figure A.2.55. Job plot showing the relative integrations versus the measured mole fraction of (*R*,*R*)-TMCDA for 0.20 M **6** and 1.0 M total (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA in toluene recorded at −80 °C.
L = (*R*,*R*)-TMCDA, L' = (*S*,*S*)-TMCDA.

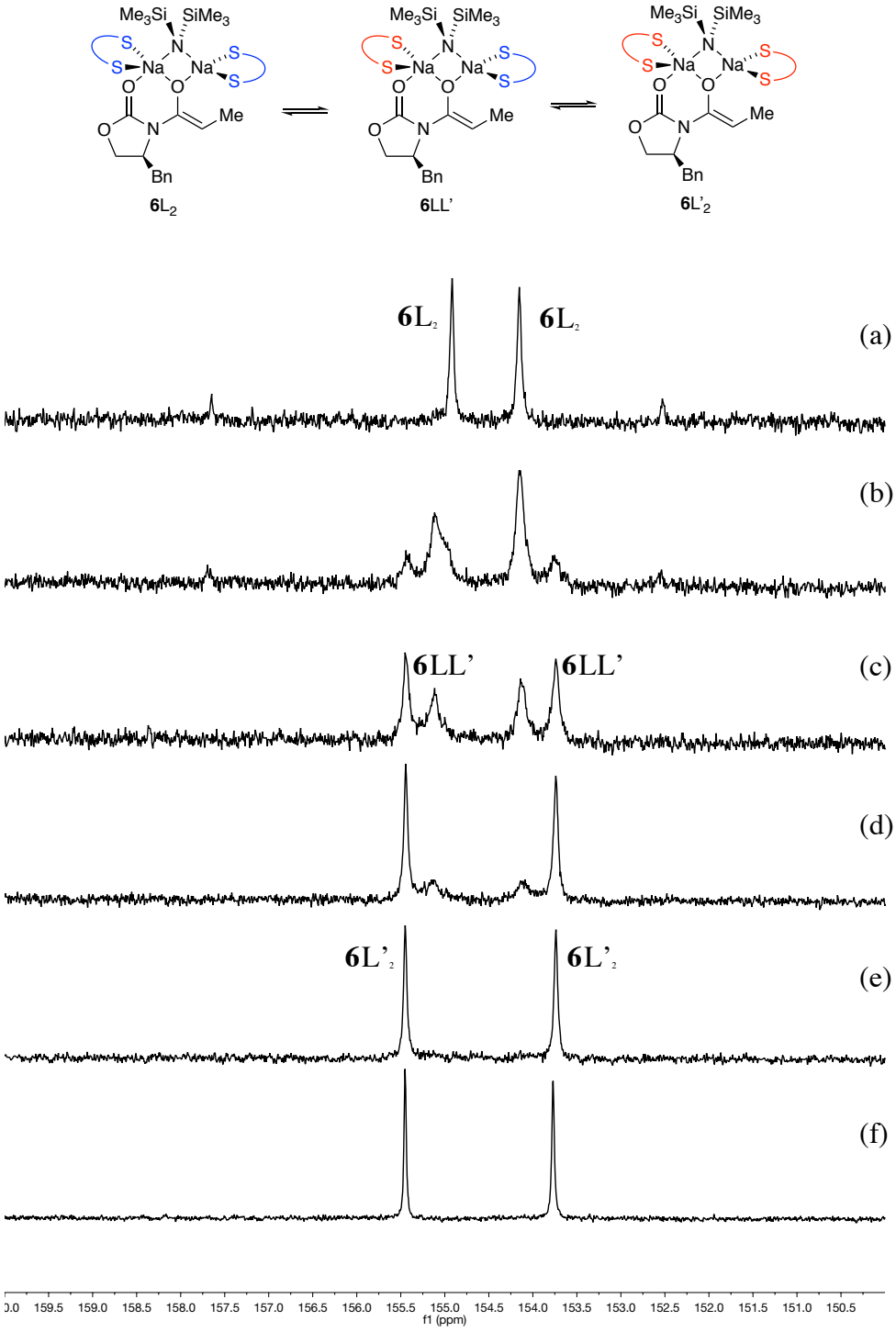


Figure A.2.56. ^{13}C NMR spectra of 0.20 M **6** and 1.0 M (*R*,*R*)-TMCDA and TMEDA in toluene recorded at –80 °C. The intended mole fractions for TMEDA, X_B, in (a)–(f) are 0.00, 0.20, 0.40, 0.60, 0.80, and 1.00, respectively. L = (*R*,*R*)-TMCDA, L' = TMEDA.

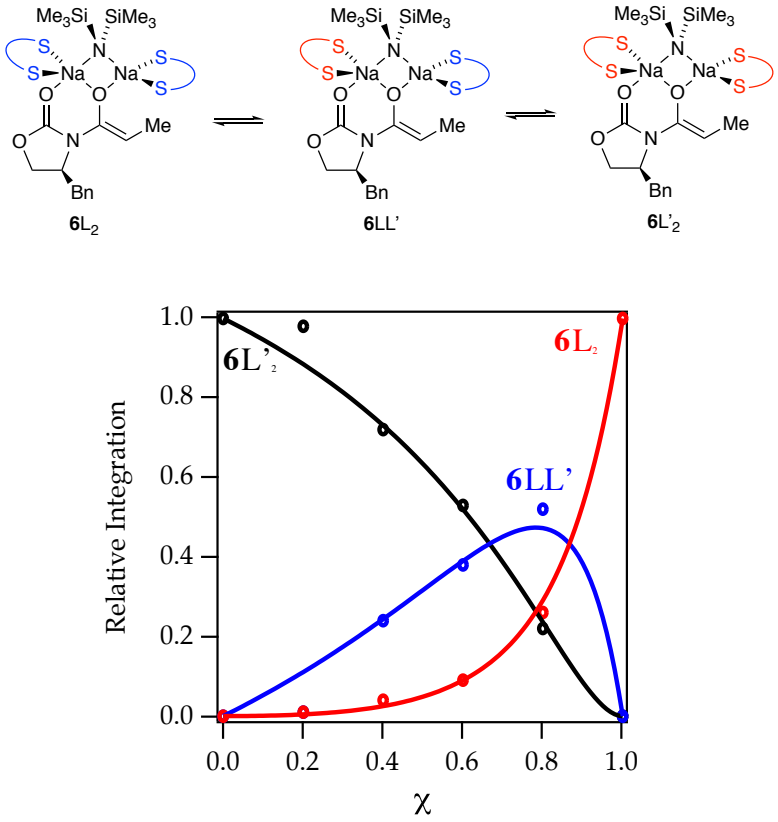


Figure A.2.57. Job plot showing the relative integrations versus the intended mole fraction of TMEDA for 0.20 M **6** and 1.0 M total (*R*,*R*)-TMCDA and TMEDA in toluene recorded at −80 °C. The offset of the maximum to the right shows a relative preference for binding (*S*,*S*)-TMCDA versus (*R*,*R*)-TMCDA. L = (*R*,*R*)-TMCDA, L' = TMEDA.

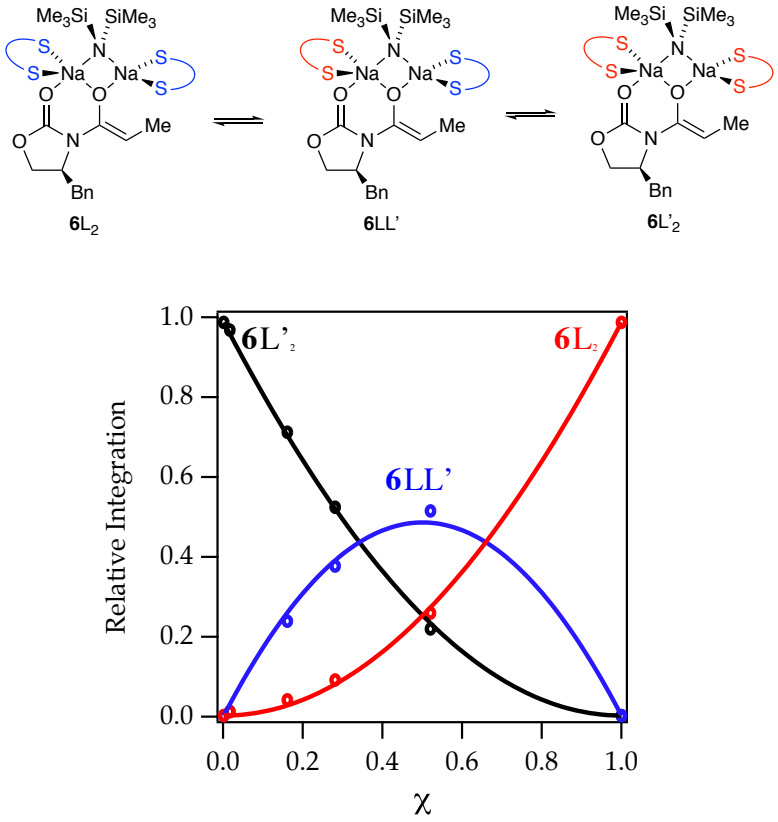


Figure A.2.58. Job plot showing the relative integrations versus the measured mole fraction of TMEDA for 0.20 M **6** and 1.0 M total (*R*,*R*)-TMCDA and TMEDA in toluene recorded at −80 °C. The absence of data on the right half arises from strong binding affinity TMEDA has much stronger binding affinity to the mixed dimer (*R*,*R*)-TMCDA. L = (*R*,*R*)-TMCDA, L' = TMEDA.

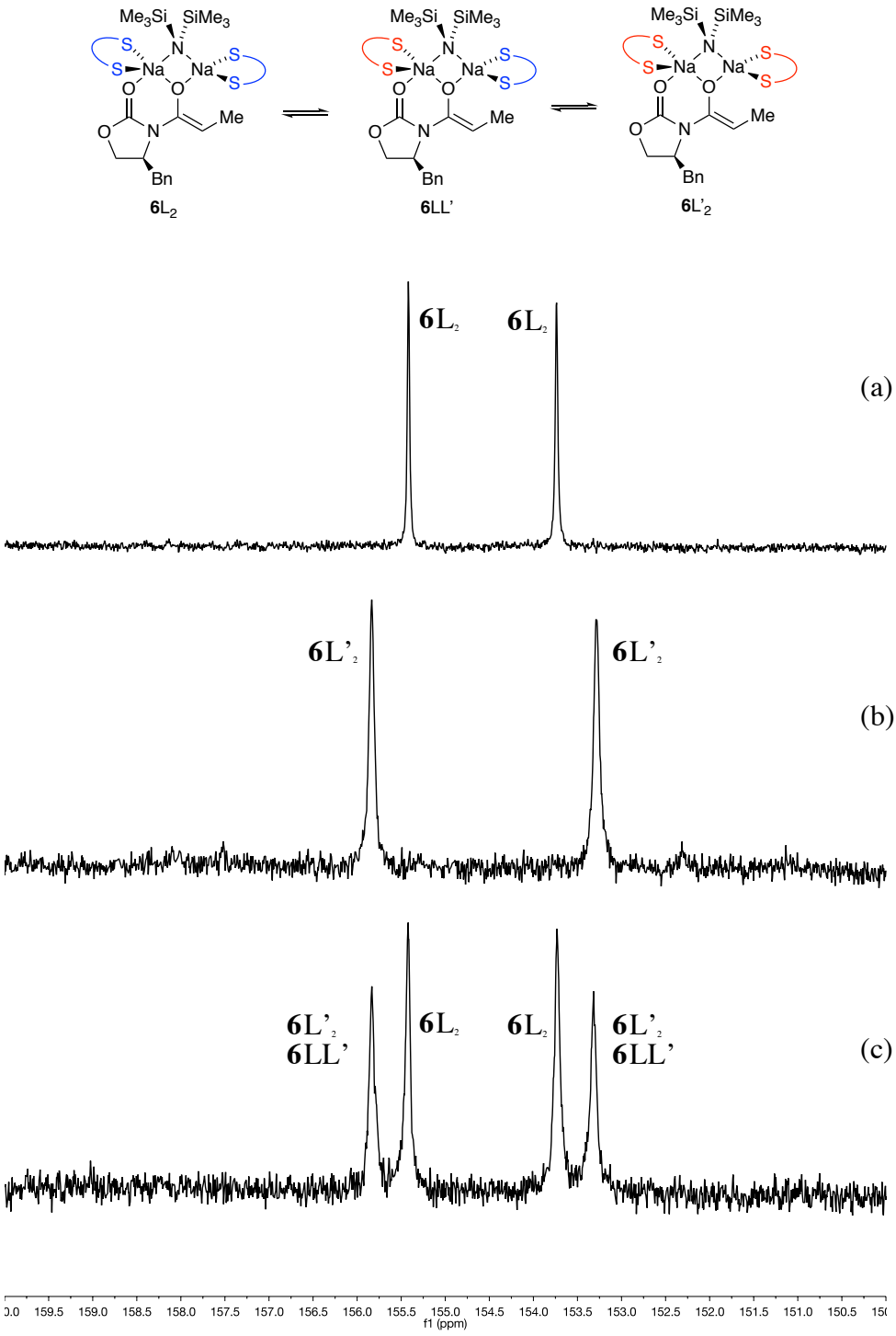


Figure A.2.59. ^{13}C NMR spectra of 0.20 M **6** in (a) 1.0 M TMEDA; (b) 1.0 M (*S*,*S*)-TMCDA; (c) 0.5 M TMEDA and 0.5 M (*S*,*S*)-TMCDA in toluene recorded at –80 °C. A mixed solvate is not observed because, presumably owing to resonance overlaps.L = TMEDA, L' = (*S*,*S*)-TMCDA.

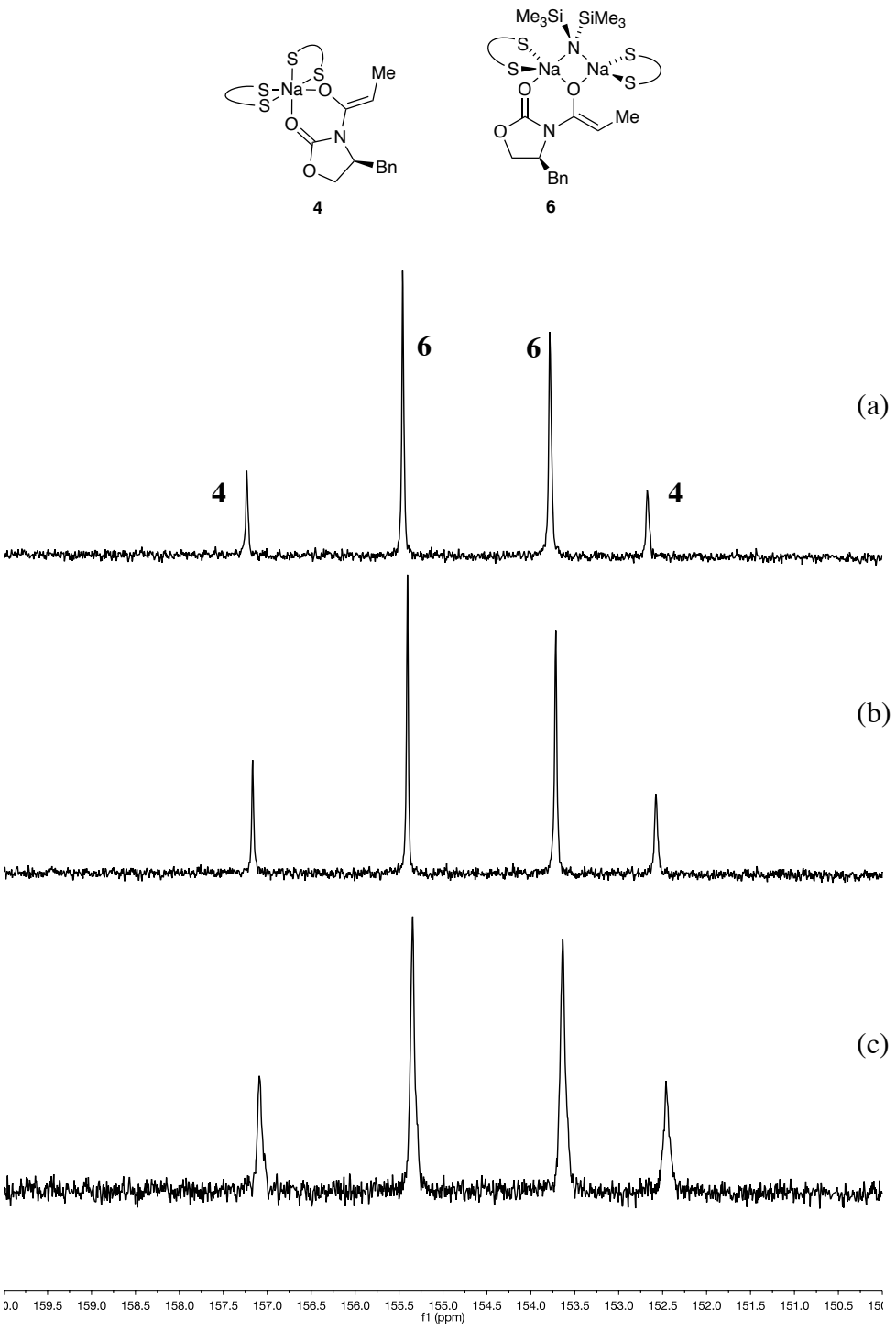


Figure A.2.60. ^{13}C NMR spectra of 0.10 M **4**, 0.10 M **6** and (a) 0.80 M TMEDA; (b) 1.8 M TMEDA; (c) 3.0 M TMEDA in toluene recorded at –80 °C.Adding more TMEDA to a mixture of monomer and NaHMDS mixed dimer shows no ratio change because the equilibrium favoring mixed dimer is essentially quantitative.

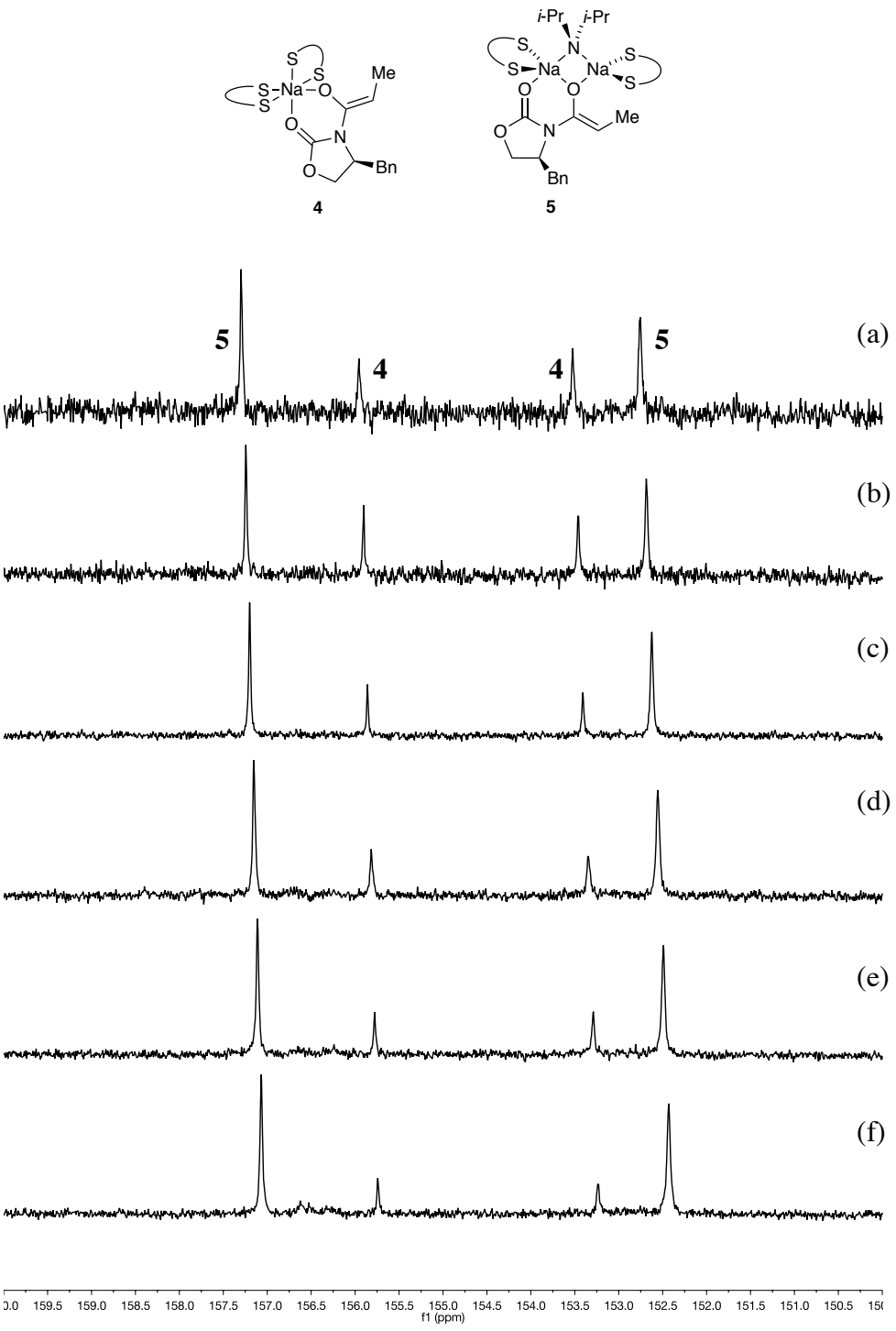


Figure A.2.61. ^{13}C NMR spectra in toluene recorded at –80 °C of 0.20 M (*S*)-**2**, 0.10 M NaDA and (a) 0.30 M TMEDA; (b) 1.0 M TMEDA; (c) 1.6 M TMEDA; (d) 2.3 M TMEDA; (e) 3.0 M TMEDA; (f) 3.6 M TMEDA.

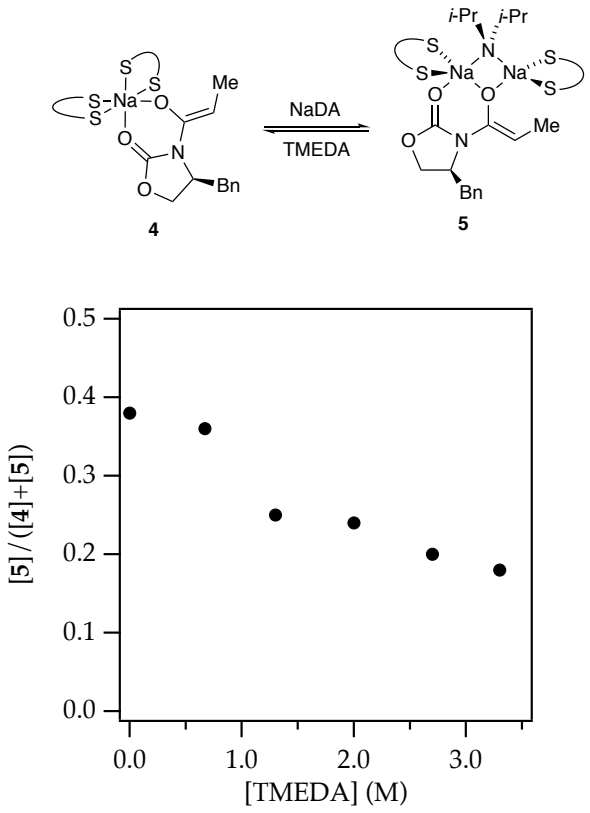


Figure A.2.62. Plot of mixed dimer **5** proportion versus [TMEDA] in a solution of 0.20 M (*S*)-**2** and 0.10 M NaDA in TMEDA/toluene at –80 °C. Data are from Figure A.2.61. The NaDA mixed dimer/monomer ratio decreases when raising the concentration of TMEDA, suggesting a lower per-sodium solvation number on the mixed dimer.

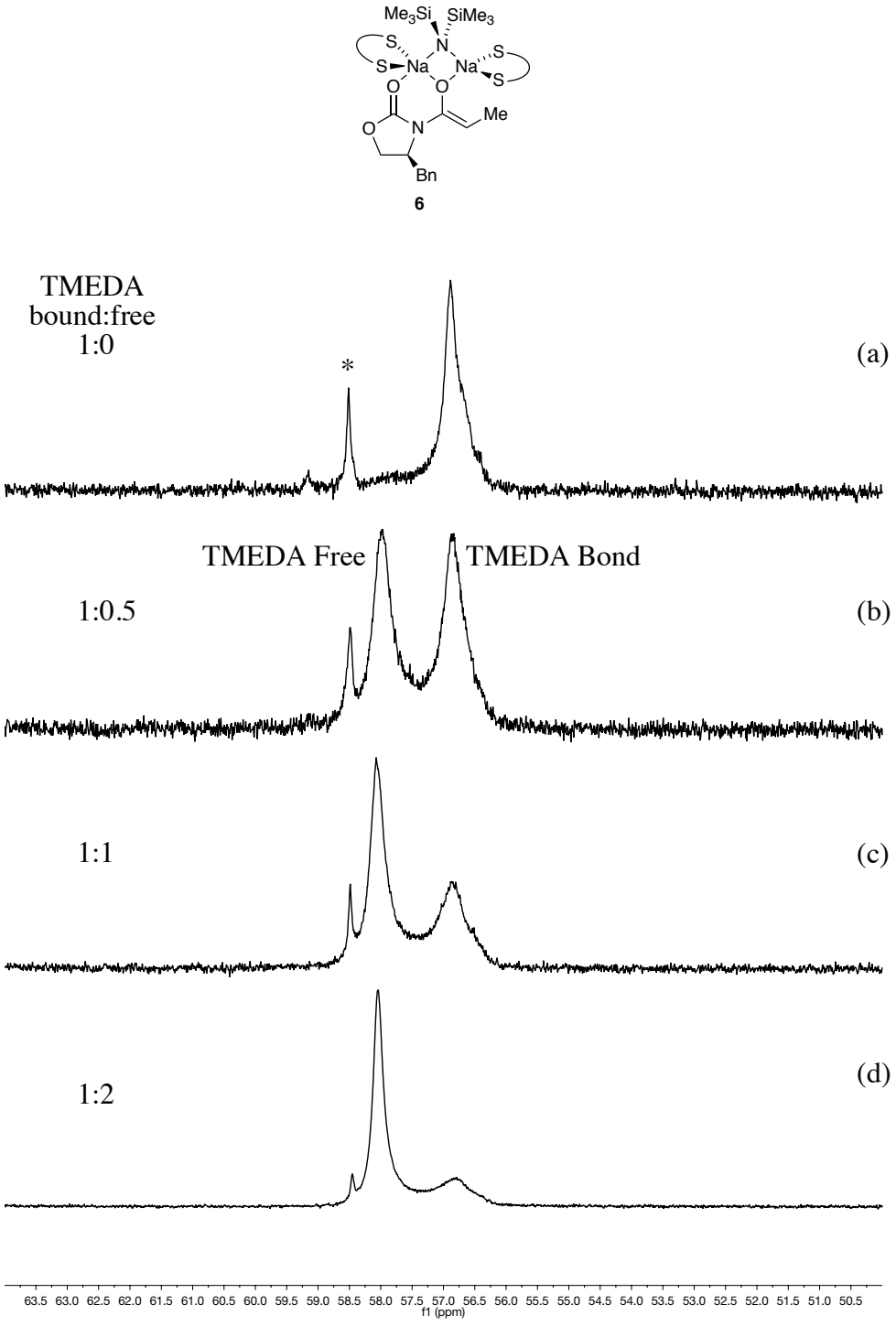


Figure A.2.63. ^{13}C NMR spectra in toluene recorded at –80 °C of 0.20 M **6**: (a) 0.40 M TMEDA; (b) 0.60 M TMEDA; (c) 0.80 M TMEDA; (d) 1.2 M TMEDA. The ratio of free and bound TMEDA is qualitatively consistent with one ligand per sodium.
*Oxazolidinone methine carbon adjacent to nitrogen.

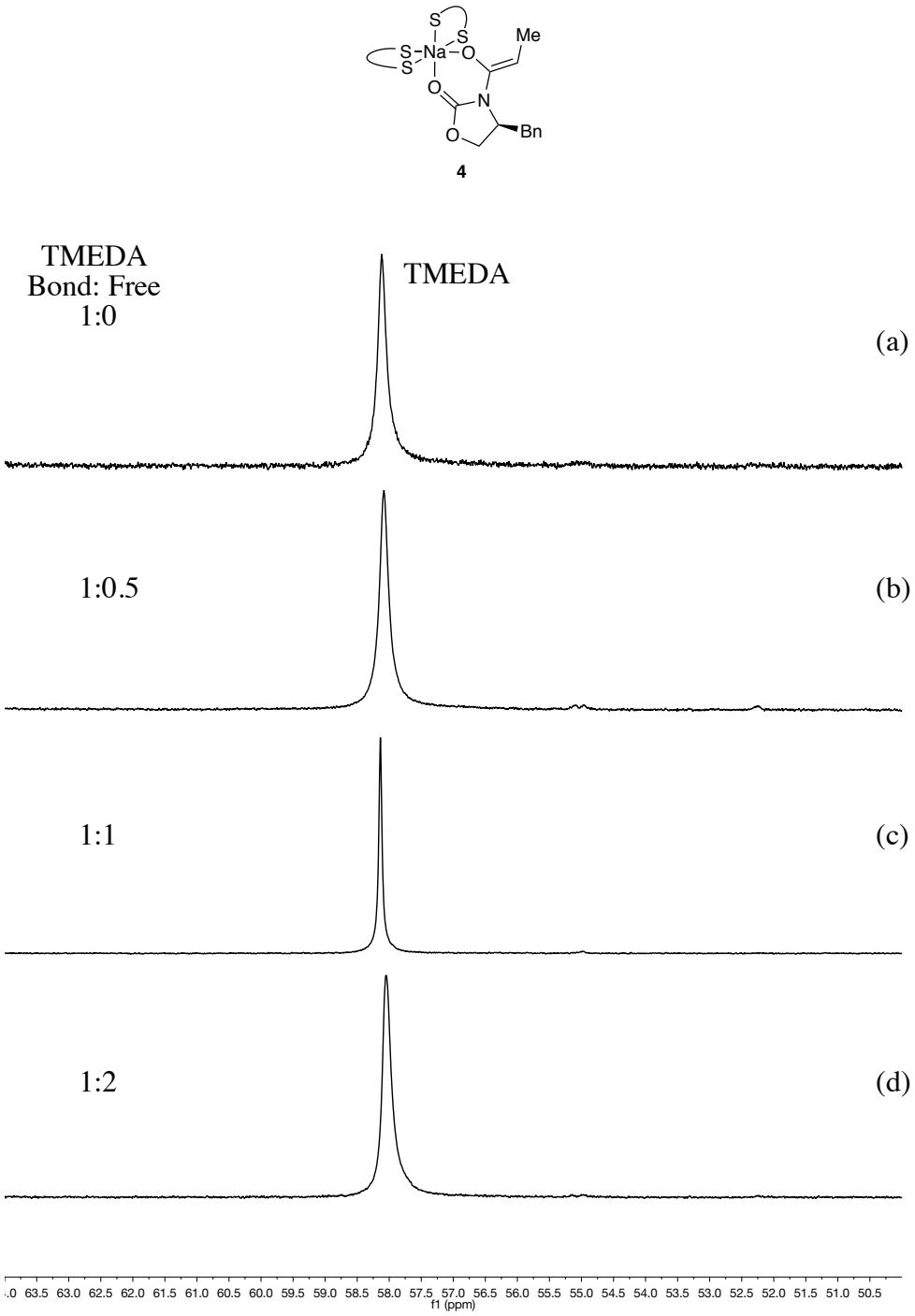


Figure A.2.64. ^{13}C NMR spectra in toluene recorded at –80 °C of 0.20 M **4** and (a) 0.40 M TMEDA; (b) 0.60 M TMEDA; (c) 0.80 M TMEDA; (d) 1.2 M TMEDA. Free and monomer-bound TMEDA do not resolve.

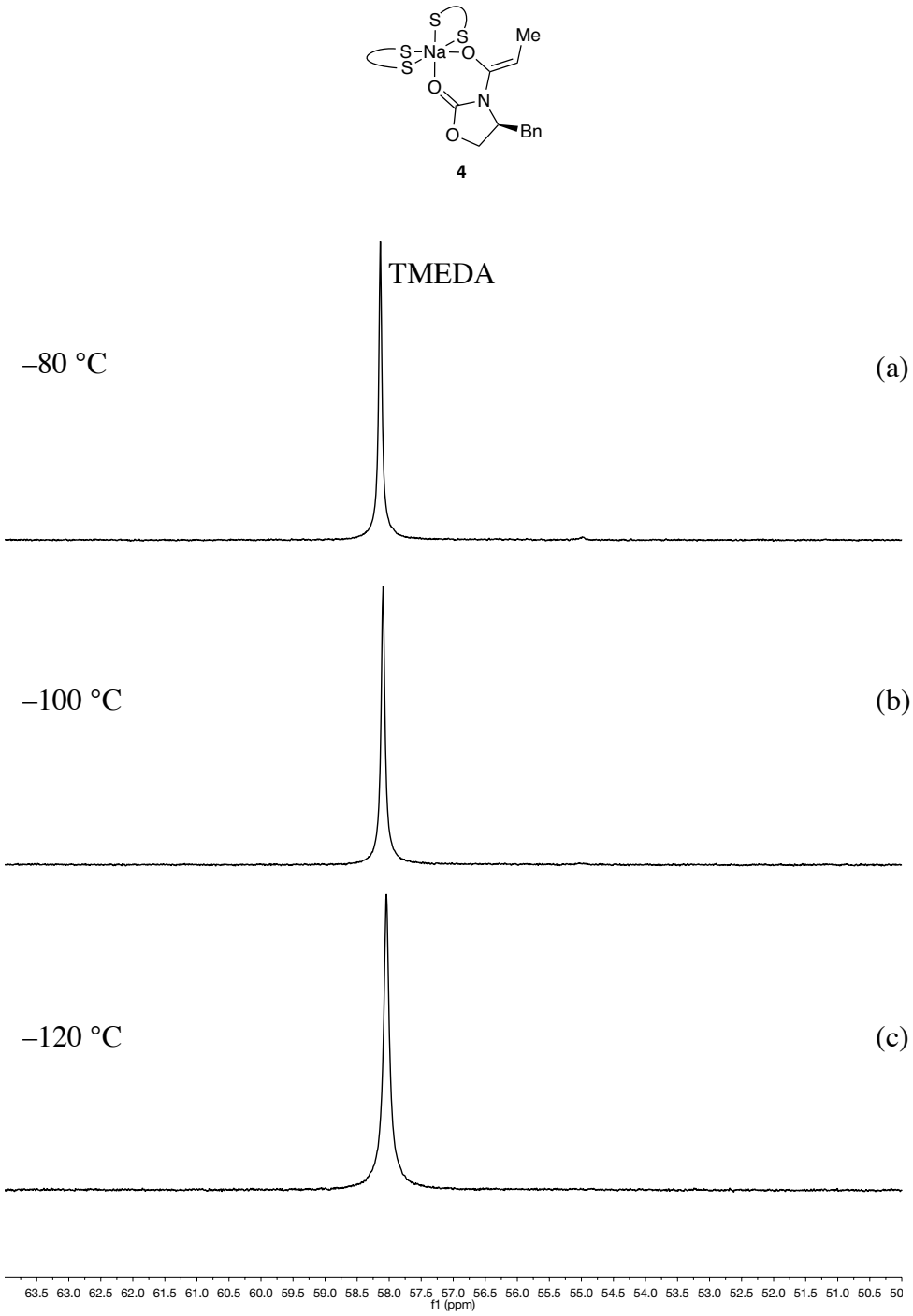


Figure A.2.65. ^{13}C NMR spectra of 0.20 M **4** and 0.80 M TMEDA in 25% cyclopentane/toluene recorded at (a) –80 °C; (b) –100 °C; (c) –120 °C. Cooling the solution does not resolve the free and monomer-bound TMEDA.

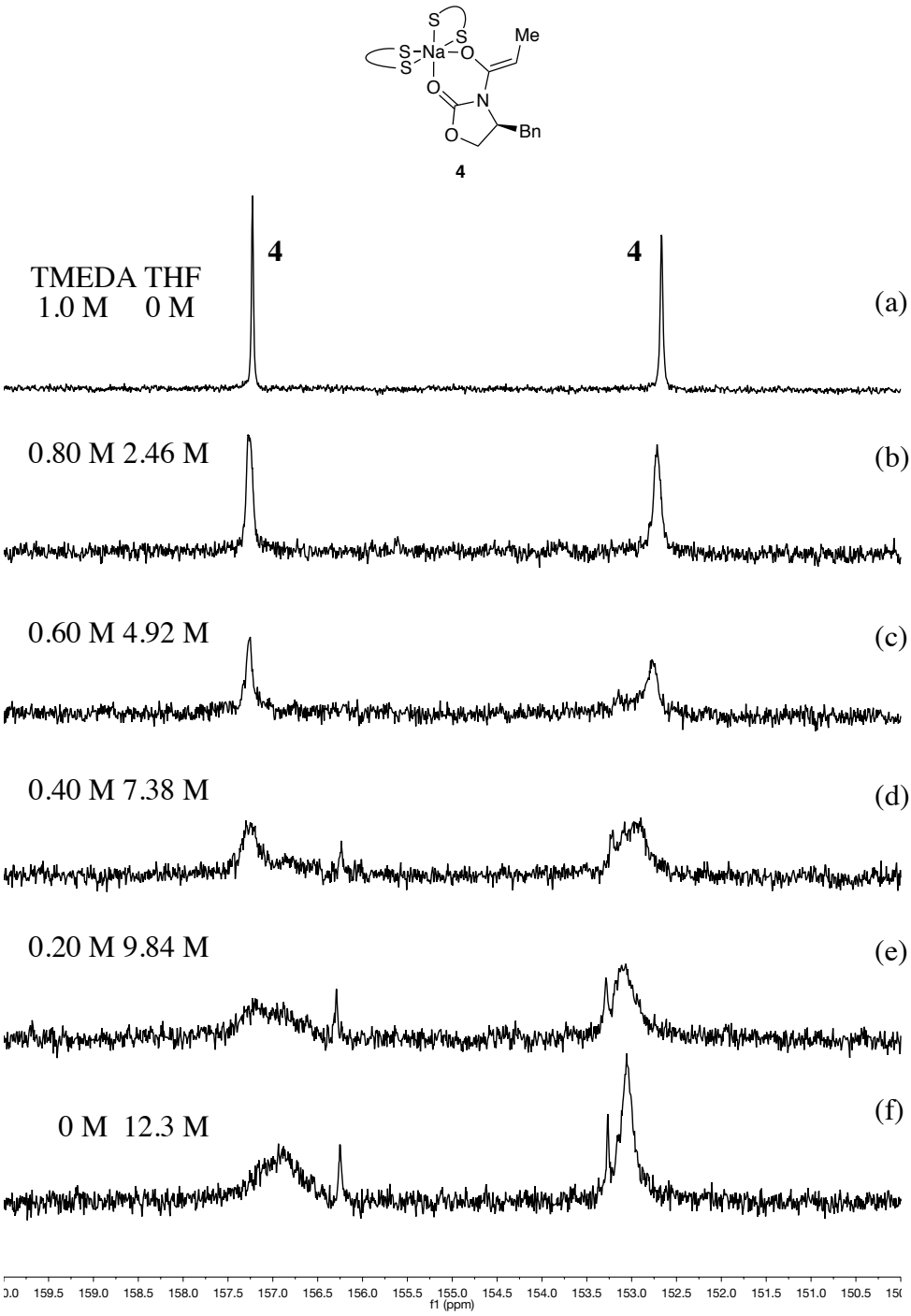


Figure A.2.66. ^{13}C NMR spectra in toluene co-solvent recorded at –80 °C of 0.20 M **4** and (a) 1.0 M TMEDA; (b) 0.80 M TMEDA and 2.46 M THF; (c) 0.60 M TMEDA and 4.92 M THF; (d) 0.40 M TMEDA and 7.38 M THF; (e) 0.20 M TMEDA and 9.84 M THF; (f) 12.3 M THF. Gradually switching from a TMEDA/toluene solvent system to THF significantly lowers the quality of the spectra.

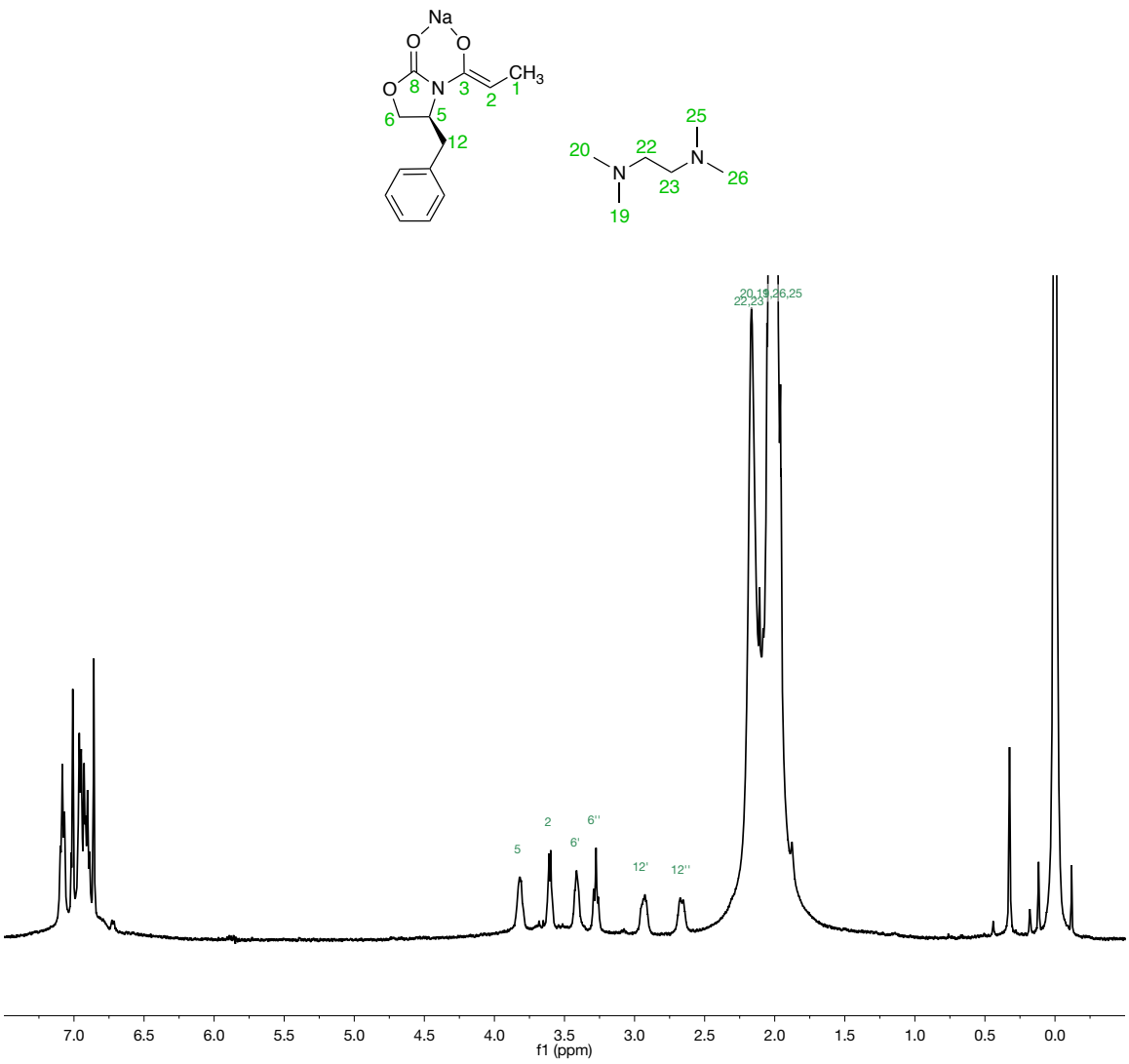


Figure A.2.67. ^{1}H NMR spectrum of 0.20 M **4** in 0.50 M TMEDA/toluene recorded at –60 °C. The peaks are assigned by an HSQC experiment.

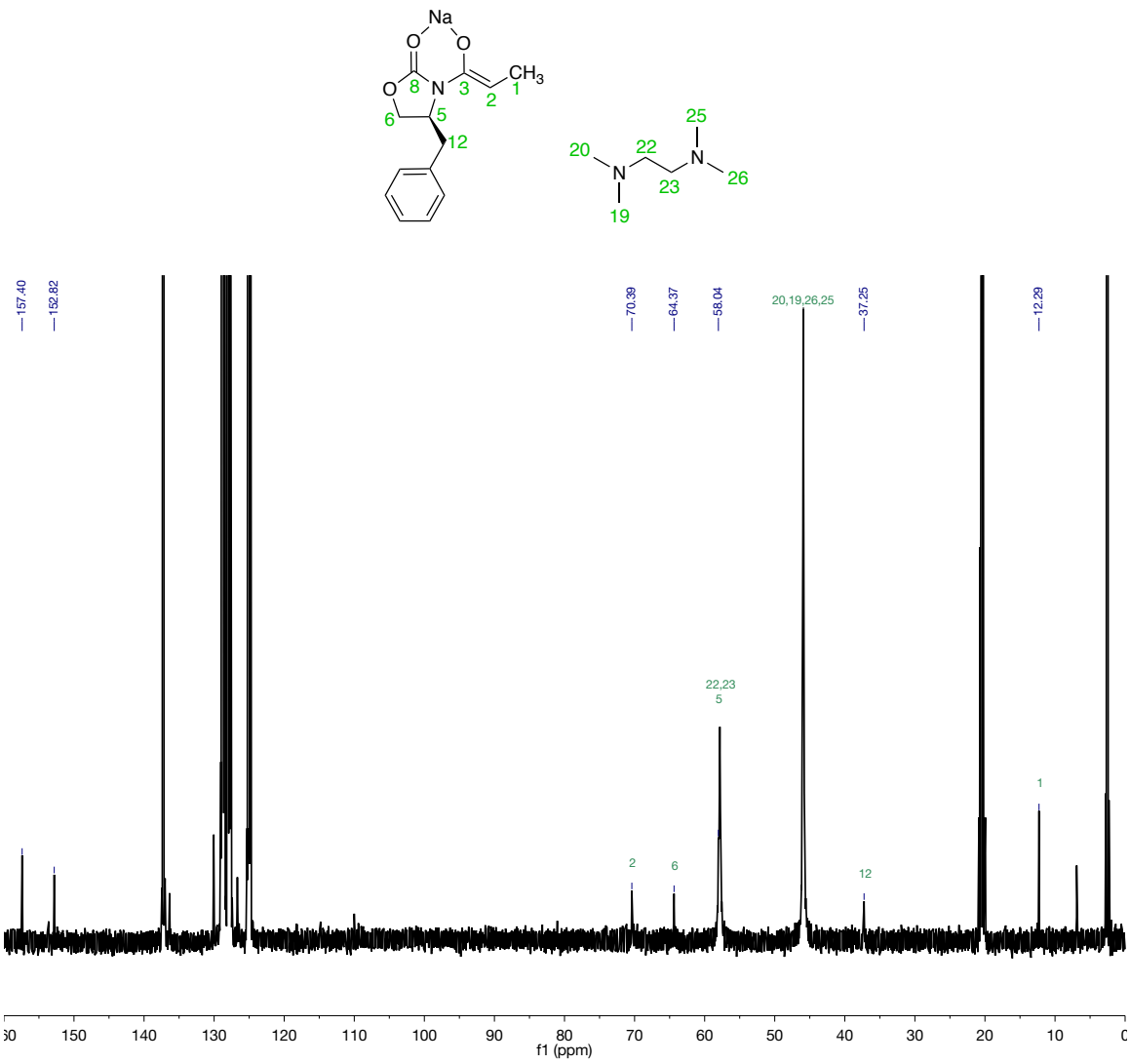


Figure A.2.68. ^{13}C NMR spectrum of 0.20 M **4** in 0.50 M TMEDA/toluene recorded at –60 °C.

Parameter	Value
1 Solvent	toluene
2 Temperature	-60.0
3 Pulse Sequence	gHSQCAD
4 Number of Scans	2
5 Receiver Gain	30
6 Relaxation Delay	1.0000
7 Pulse Width	7.5000
8 Acquisition Time	0.1499

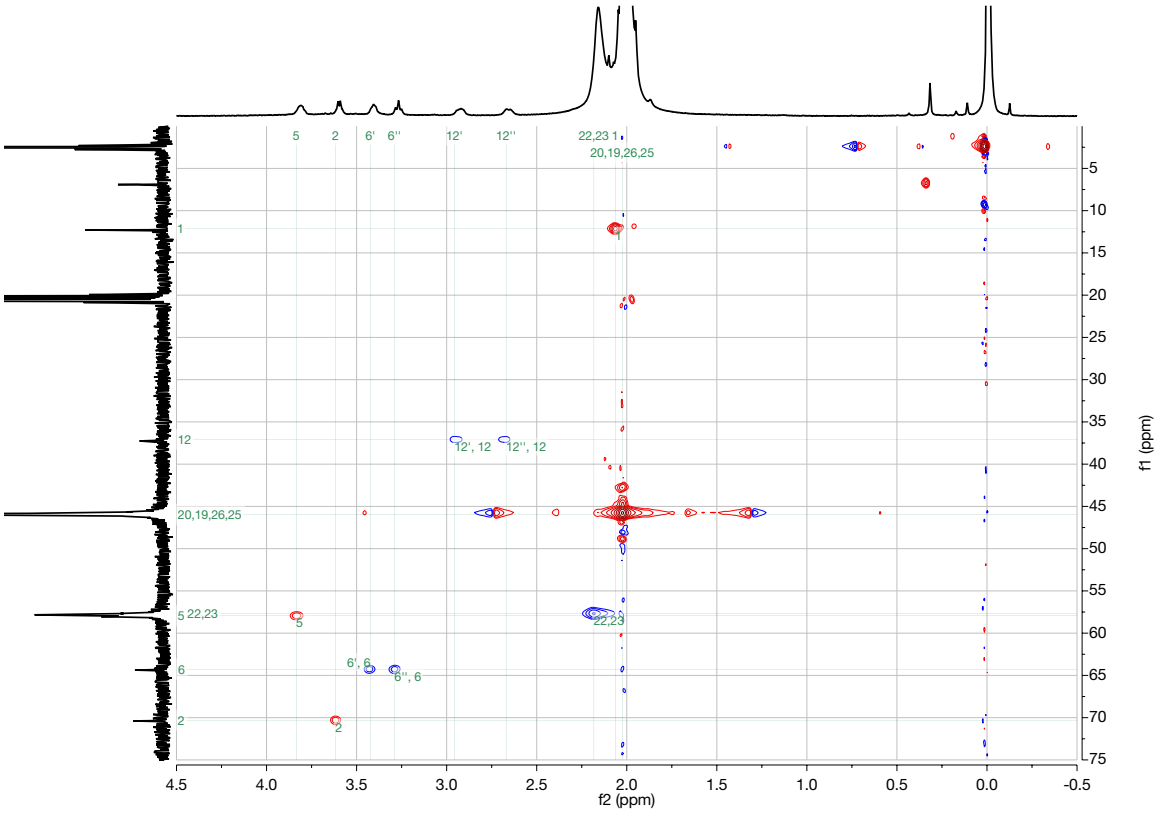


Figure A.2.69. HSQC spectrum of 0.20 M **4** in 0.50 M TMEDA/toluene recorded at –60 °C.

Parameter	Value
1 Solvent	toluene
2 Temperature	-60.0
3 Pulse Sequence	ROESYAD
4 Number of Scans	2
5 Receiver Gain	0
6 Relaxation Delay	1.0000
7 Pulse Width	7.5000
8 Acquisition Time	0.4001

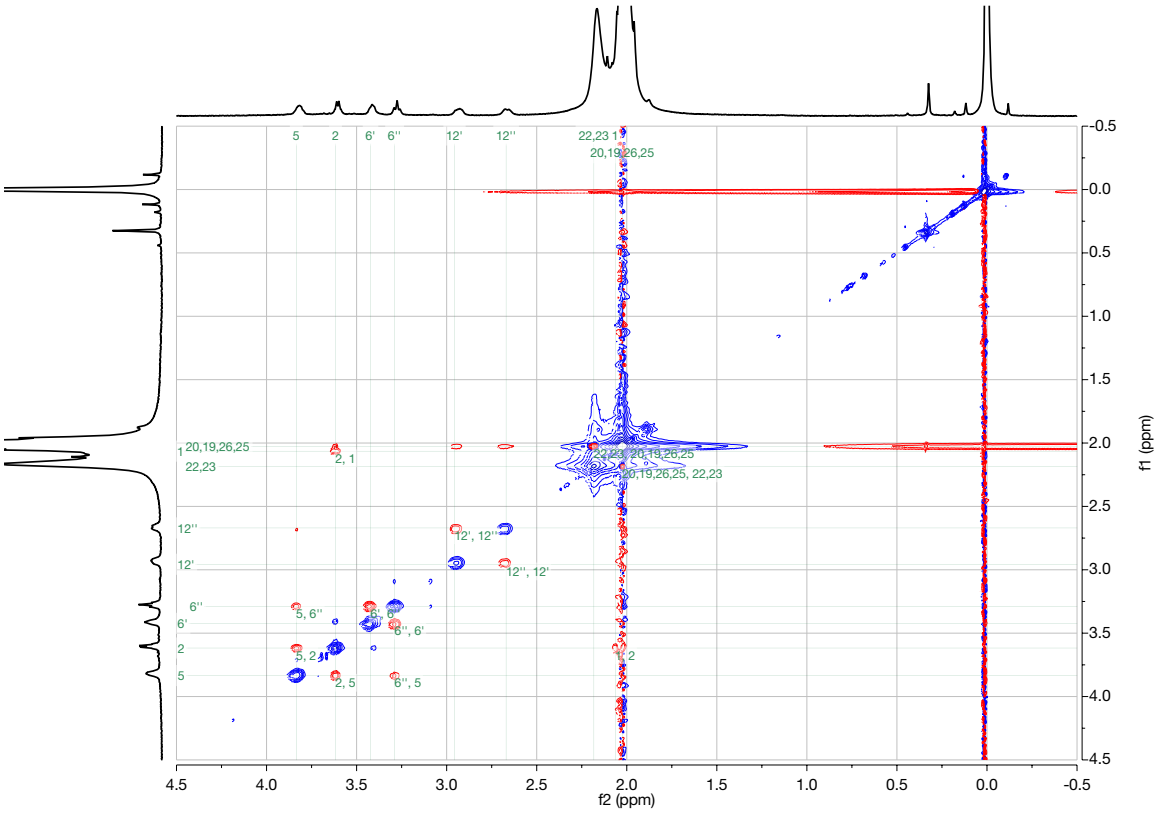


Figure A.2.70. ROESY spectrum of 0.20 M **4** in 0.50 M TMEDA/toluene recorded at –60 °C.

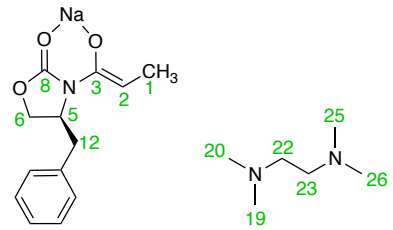


Table A.2.1. ^{1}H and ^{13}C chemical shift assignments for monomer **4**.

Atom #	δC, ppm	δH, ppm	ROESY
1	12.13	2.06	2
2	70.29	3.62	1, 5, 19
3	152.82	-	-
5	57.93	3.83	2, 6”
6	64.26	3.42 (6’)	6”
		3.29 (6”)	5, 6’
8	157.40	-	
12	37.08	2.96 (12’)	12”, 19
		2.67 (12”)	12’, 19
19, 20, 25, 26	45.93	2.03	2, 12’, 12”, 22
22, 23	57.68	2.18	19

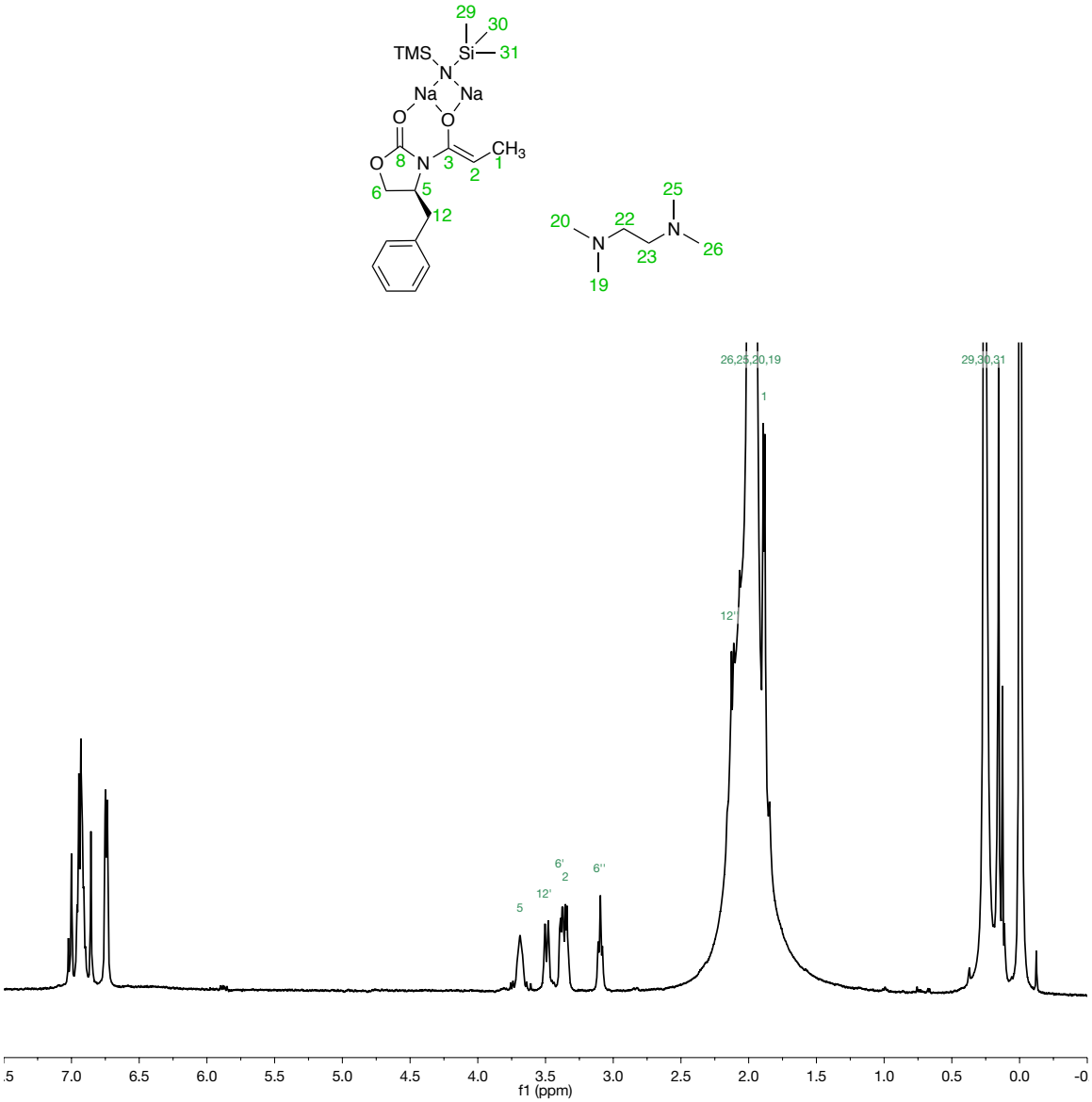


Figure A.2.71. ^{1}H NMR spectrum of 0.20 M **6** in 1.0 M TMEDA/toluene recorded at –60 °C.

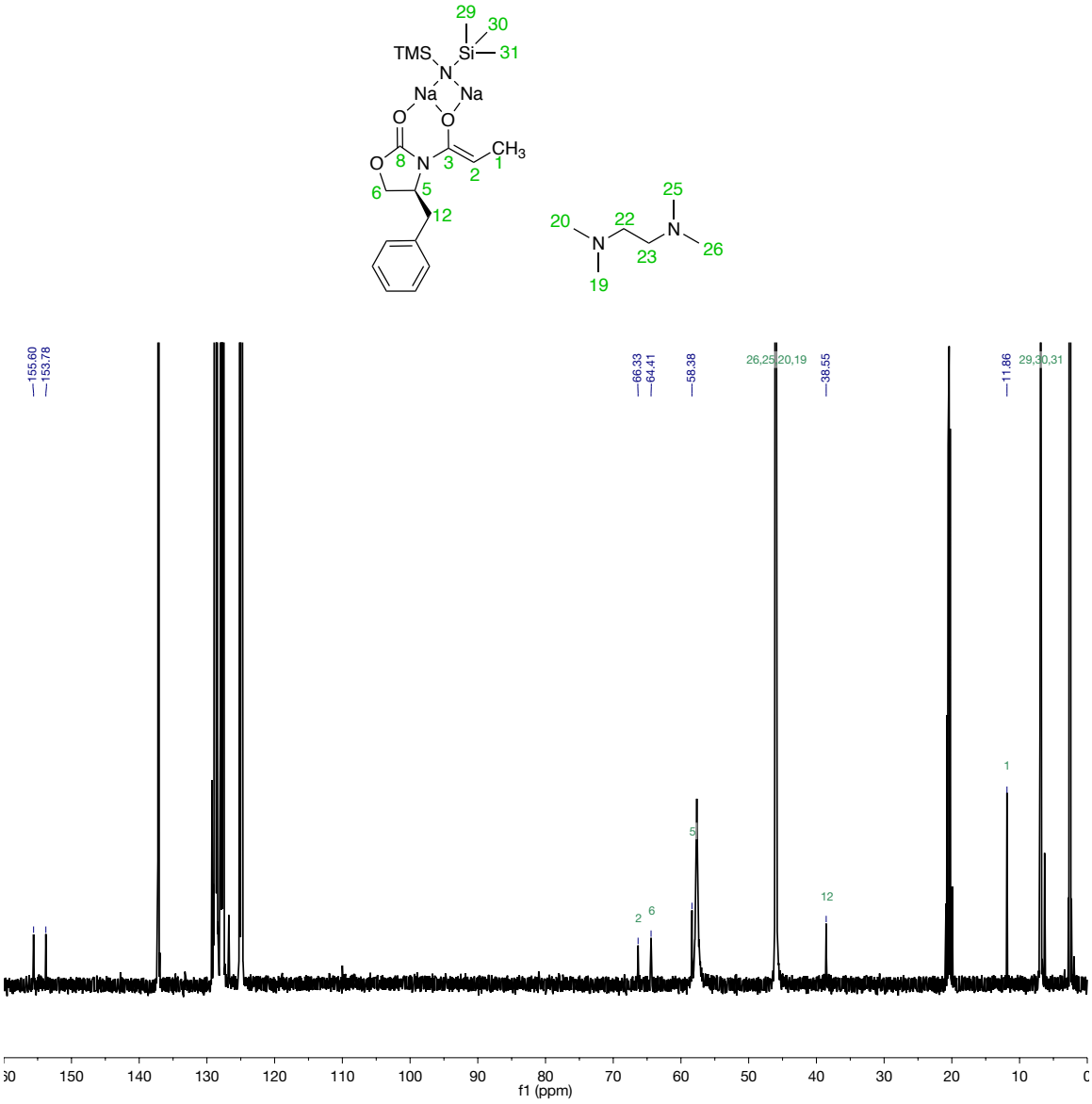
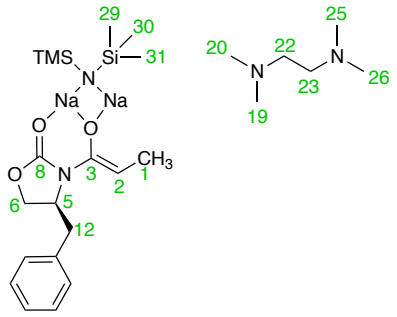


Figure A.2.72. ^{13}C NMR spectrum of 0.20 M **6** in 1.0 M TMEDA/toluene recorded at –60 °C.

Parameter	Value
1 Solvent	toluene
2 Temperature	-60.0
3 Pulse Sequence	gHSQCAD
4 Number of Scans	2
5 Receiver Gain	30
6 Relaxation Delay	1.0000
7 Pulse Width	7.5000
8 Acquisition Time	0.1499



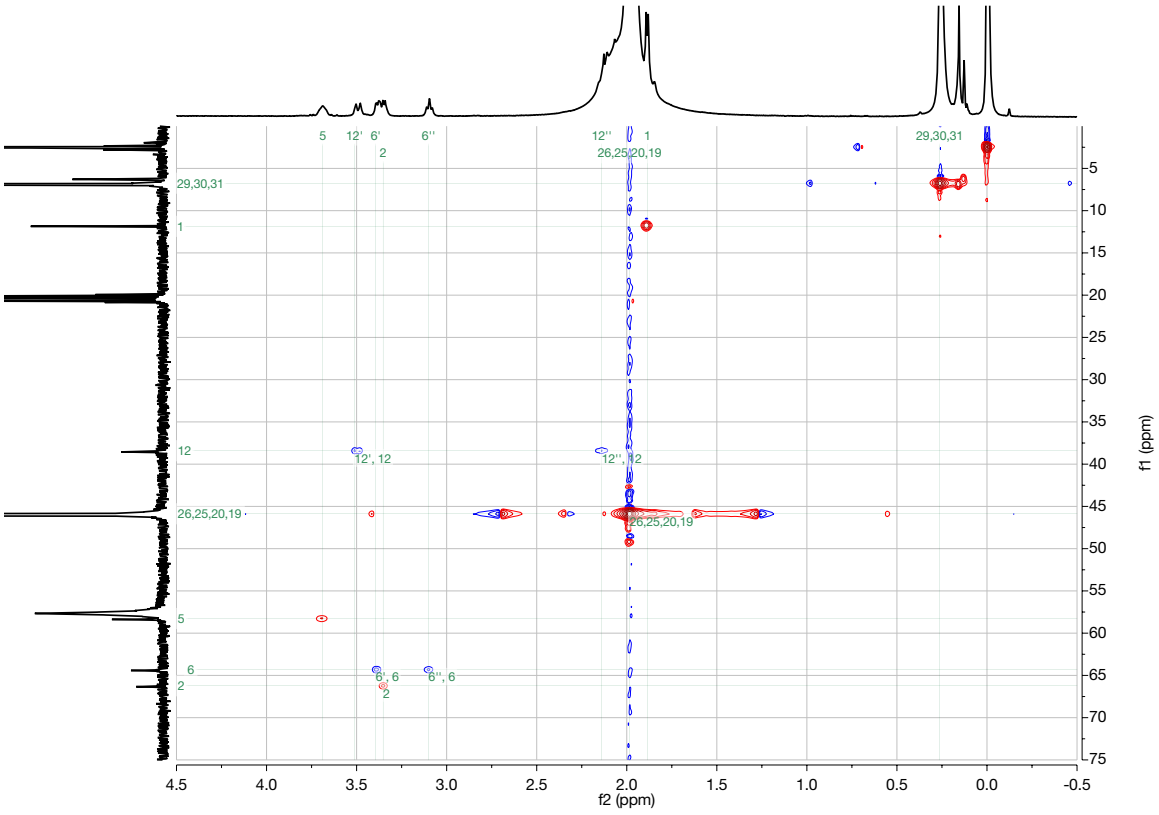
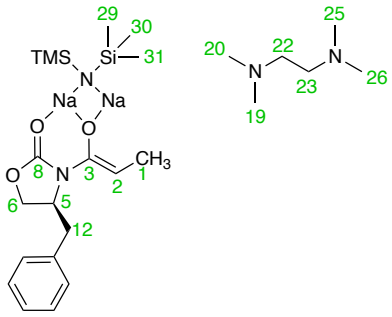


Figure A.2.73. HSQC spectrum of 0.20 M **6** in 1.0 M TMEDA/toluene recorded at –60 °C.

Parameter	Value
1 Solvent	toluene
2 Temperature	-60.0
3 Pulse Sequence	ROESYAD
4 Number of Scans	2
5 Receiver Gain	0
6 Relaxation Delay	1.0000
7 Pulse Width	7.5000
8 Acquisition Time	0.4001



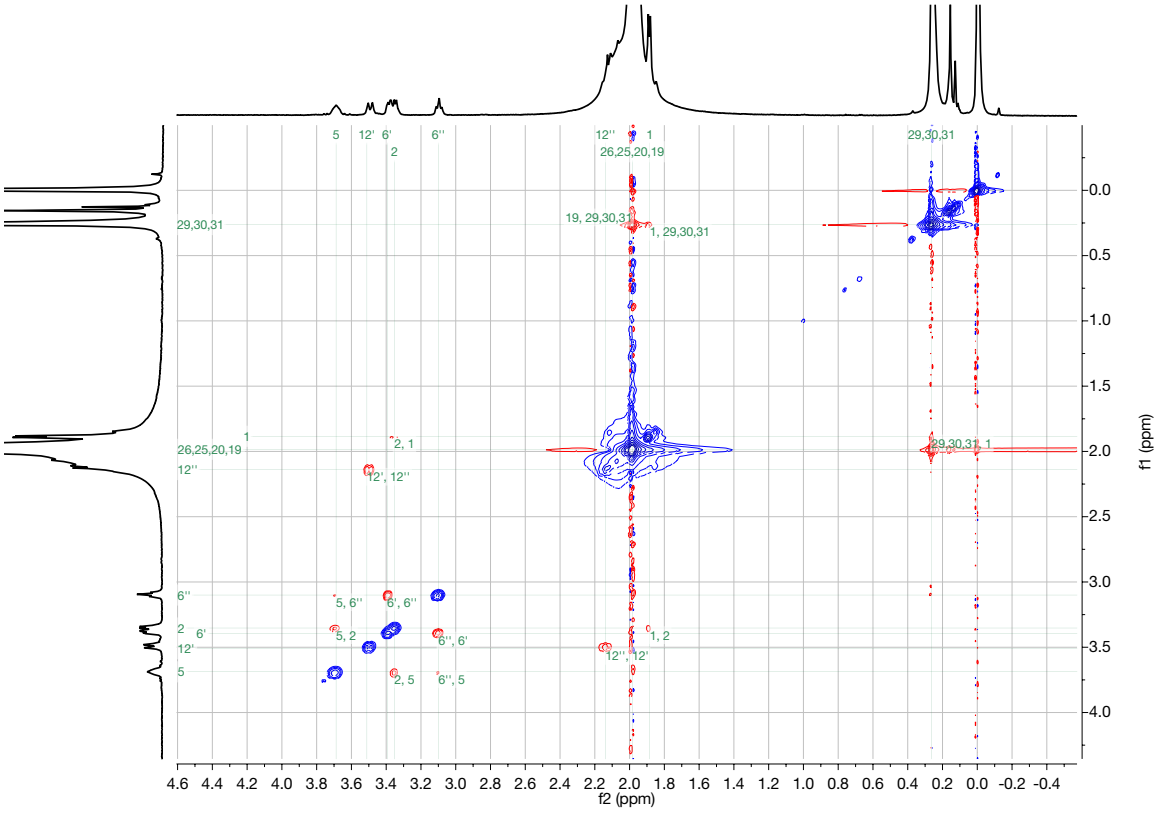


Figure A.2.74. ROESY spectrum of 0.20 M **6** in 1.0 M TMEDA/toluene recorded at –60 °C.

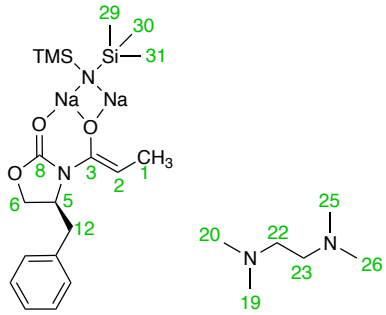


Table A.2.2. ^{1}H and ^{13}C chemical shift assignments for mix dimer **6**.

Atom #	δC, ppm	δH, ppm	ROESY
1	11.86	1.88	2, 29
2	55.23	3.35	1, 5
3	153.78	-	-
5	58.26	3.69	2, 6”
6	64.31	3.39 (6’)	6”
		3.10 (6”)	5, 6’
8	155.60	-	-
12	38.41	3.51 (12’)	12”
		2.14 (12”)	12’
19, 20, 25, 26	45.87	1.98	29
22, 23	57.66	1.98	-
29, 30, 31	6.75	0.26	1, 19

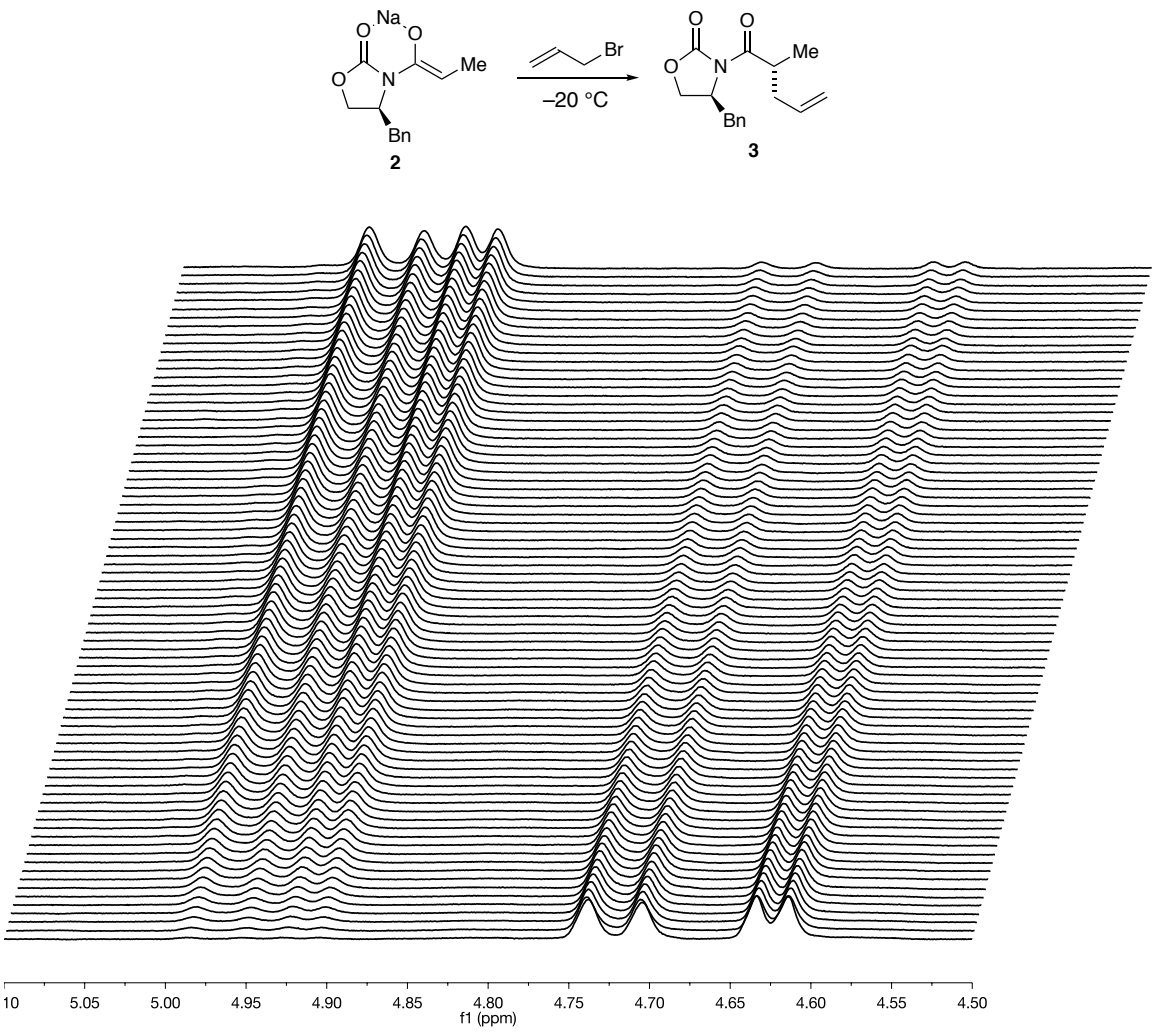


Figure A.2.75. ^{1}H NMR spectra following reaction of 0.40 M (*S*)-**2** with 0.010 M allyl bromide in 1.0 M TMEDA/toluene recorded at –20 °C at 1 spectrum per minute. The alkylation reaction is followed to completion. Both the growth of product and decay of starting material follow a first-order function.

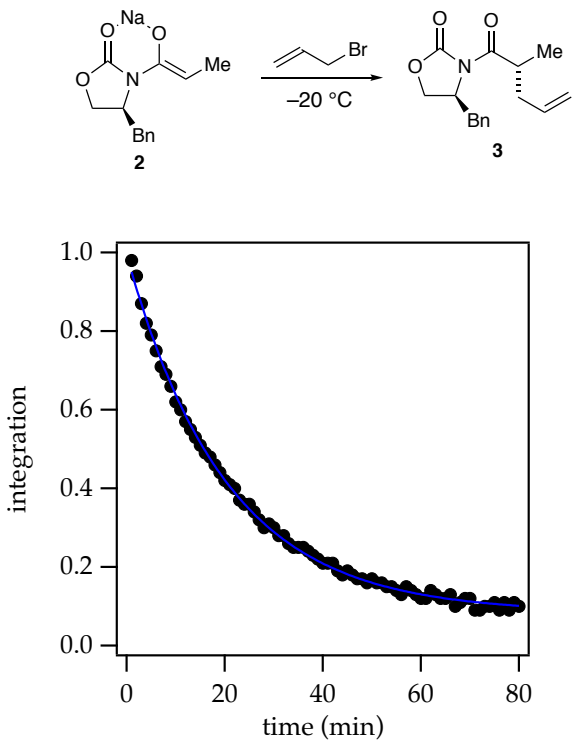


Figure A.2.76. Plot following loss of allyl bromide in 0.40 M (*S*)-**2** and 0.010 M allyl bromide in 1.0 M TMEDA/toluene at –20 °C.

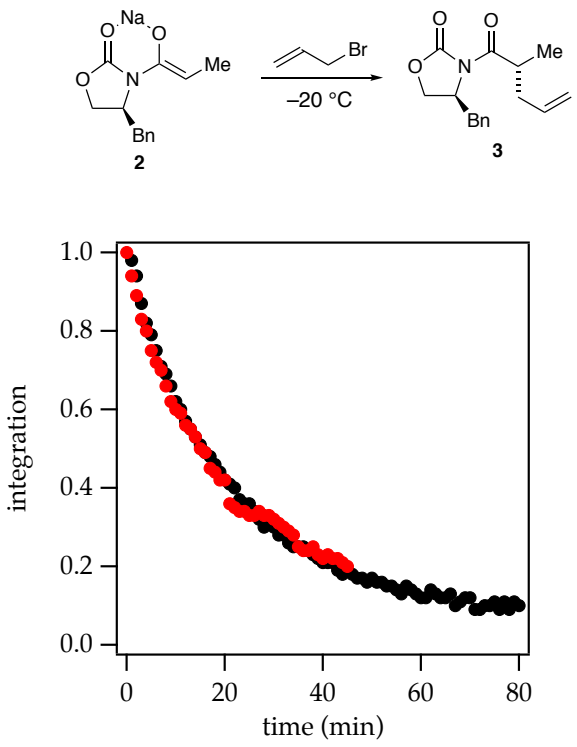


Figure A.2.77. Plot following loss of allyl bromide in 0.40 M (*S*)-**2** and second injection of 0.010 M allyl bromide in 1.0 M TMEDA/toluene at –20 °C.

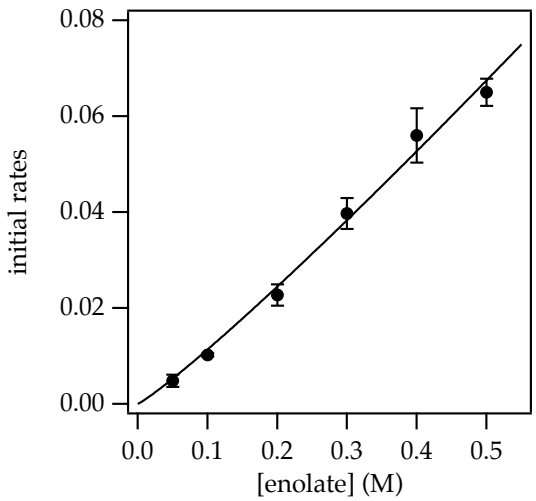


Figure A.2.78. Plot of initial rates vs [enolate]. $y = ax^n$, $a = 0.15 \pm 0.01$, $n = 1.11 \pm 0.08$. The reaction is first order in enolate.

[(*S*)-**2**] (M)	TMEDA (M)	AllylBr (M)	Run 1	Run 2
0.050	0.10	0.010	0.0039286	0.0057692
0.10	0.20	0.010	0.01	0.010455
0.20	0.40	0.010	0.024286	0.021143
0.30	0.60	0.010	0.037429	0.042
0.40	0.80	0.010	0.052	0.06
0.50	1.0	0.010	0.063	0.067

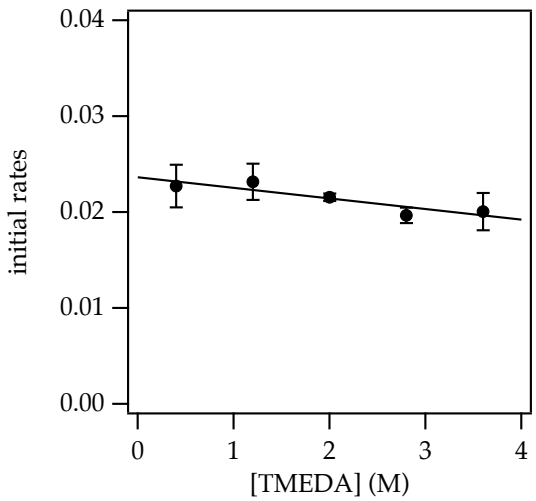


Figure A.2.79. Plot of initial rates vs [TMEDA]. $y = ax + b$, $a = -0.0011 \pm 0.0003$, $b = 0.0236 \pm 0.0007$. The reaction is zeroth order in TMEDA.

[(*S*)-**2**] (M)	TMEDA (M)	AllylBr (M)	Run 1	Run 2
0.20	0.8	0.010	0.021143	0.024286
0.20	1.6	0.010	0.0245	0.021833
0.20	2.4	0.010	0.021818	0.021273
0.20	3.2	0.010	0.019091	0.020238
0.20	4.0	0.010	0.021429	0.018667

(4S)-4-benzyl-3-((2R)-2-methylpent-4-enoyl)-2-oxazolidinone (**3**). To a solution of NaHMDS (0.60 mmol, 110 mg) and TMEDA (1.2 mmol, 180 μL) in 4.5 mL toluene under argon at –78 °C was added **1** (0.50 mmol, 116.5 mg) in 0.50 mL toluene. After stirring for 30 minutes, allyl bromide (3.0 mmol, 260 μL) was injected, and the vessel was warmed to 0 °C. The reaction was quenched by 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 20% ethyl acetate in hexanes provided 132 mg (97% yield) shown by ^{1}H NMR spectroscopy to be a 20:1 diastereomeric mixture of **3** and its isomer analogous to that reported previously. ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 5.83 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.11 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.07 (ddt, *J* = 10.1, 2.0, 1.1 Hz, 1H), 4.69 (ddt, *J* = 9.9, 7.6, 3.2 Hz, 1H), 4.19 (dd, *J* = 8.4, 7.7 Hz, 1H), 4.16 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.87 (h, *J* = 6.8 Hz, 1H), 3.29 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.70 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.53 (dtt, *J* = 13.7, 6.8, 1.3 Hz, 1H), 2.24 (dtt, *J* = 14.0, 7.0, 1.2 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.67, 153.26, 135.52, 135.41, 129.56, 129.09, 127.47, 117.37, 66.16, 55.55, 38.26, 38.13, 37.30, 16.59.

Schmidt, B.; Wildemann, H. *J. Chem. Soc., Perkin Trans. 1,* **2002**, 1050.

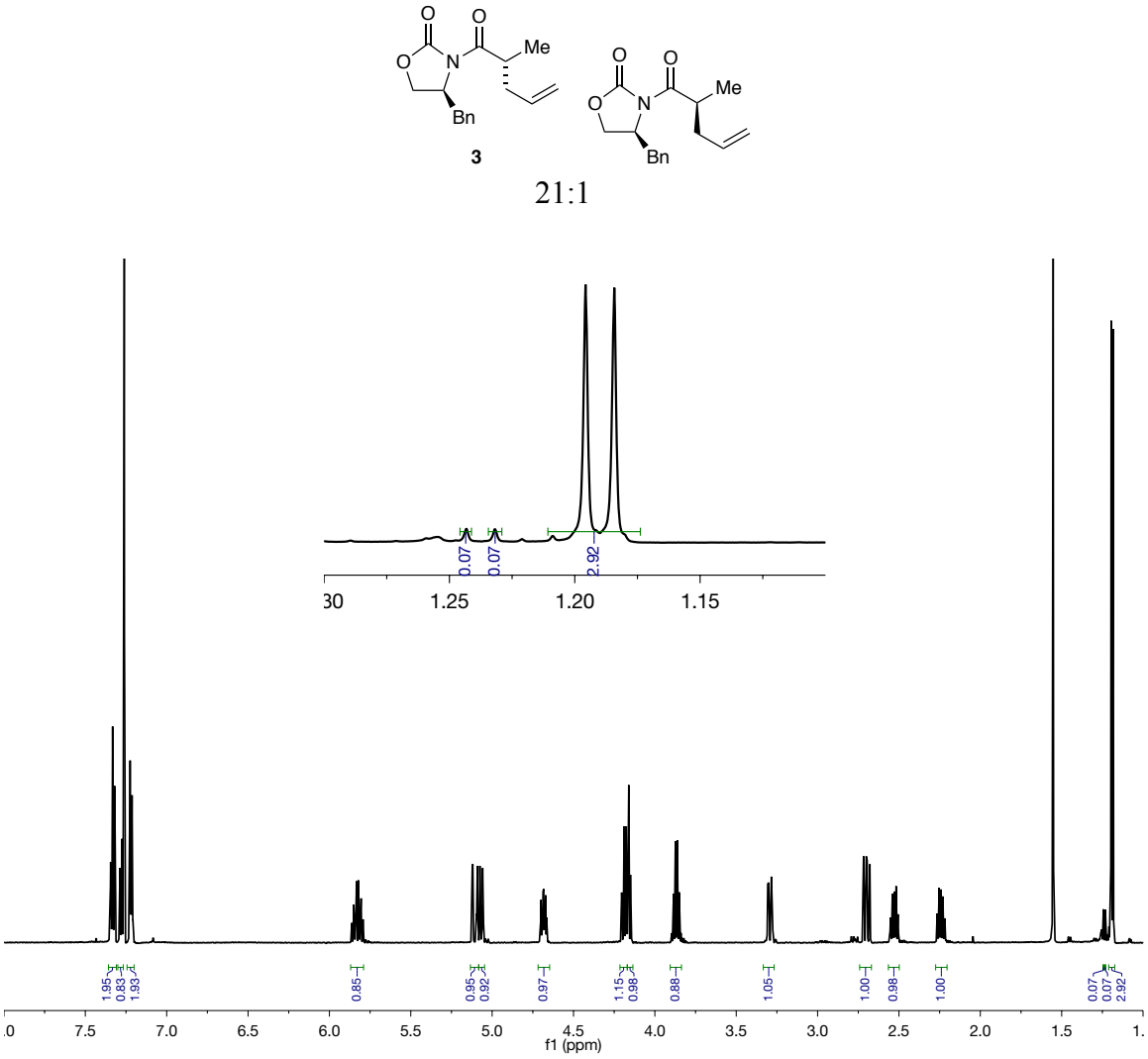


Figure A.2.80. ^{1}H NMR spectrum of **3** prepared from monomer **4** recorded in $CDCl_3$ at rt.

An isolated yield of 97% was obtained. The integration provides a selectivity of 21:1.

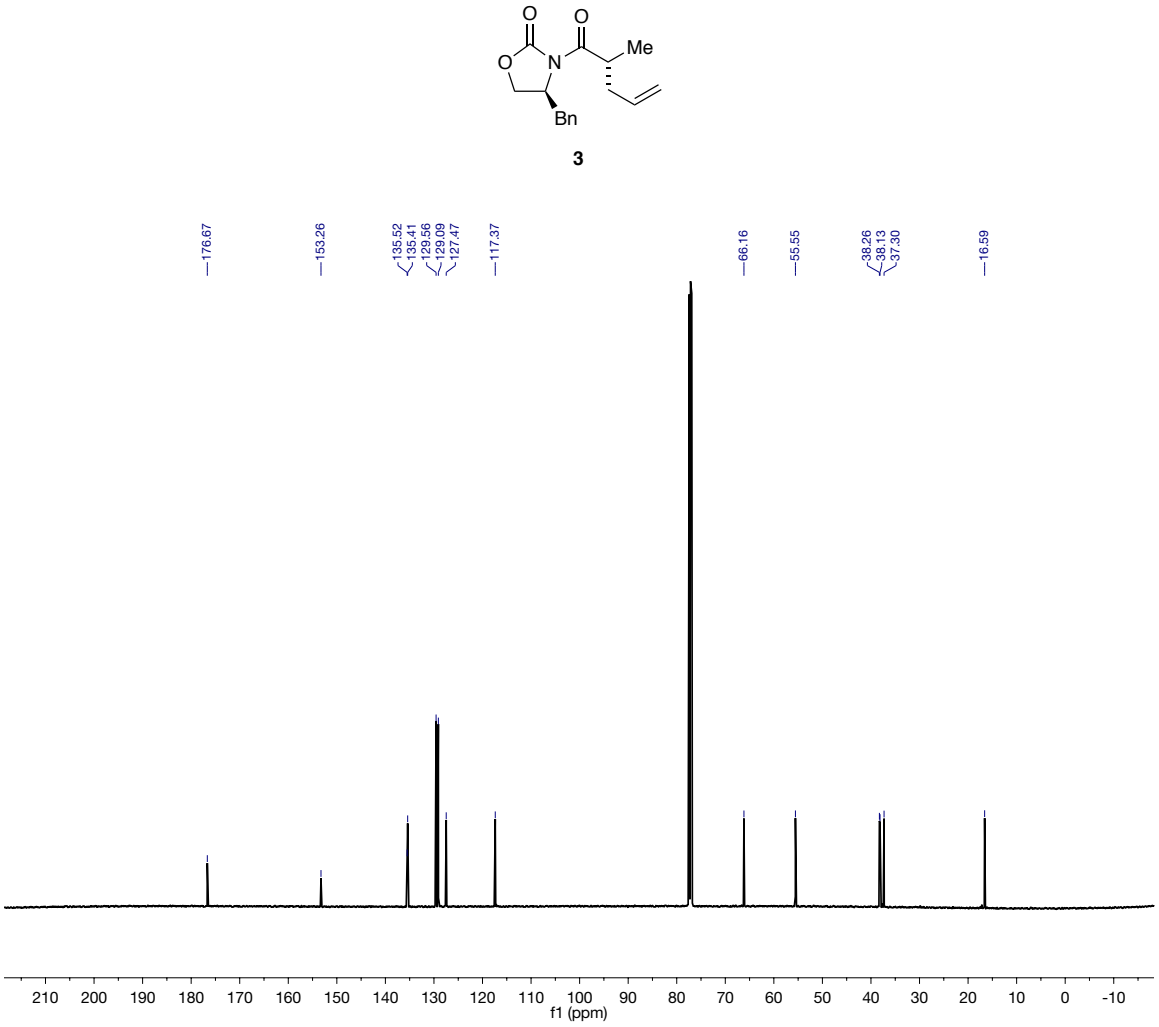


Figure A.2.81. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **3**.

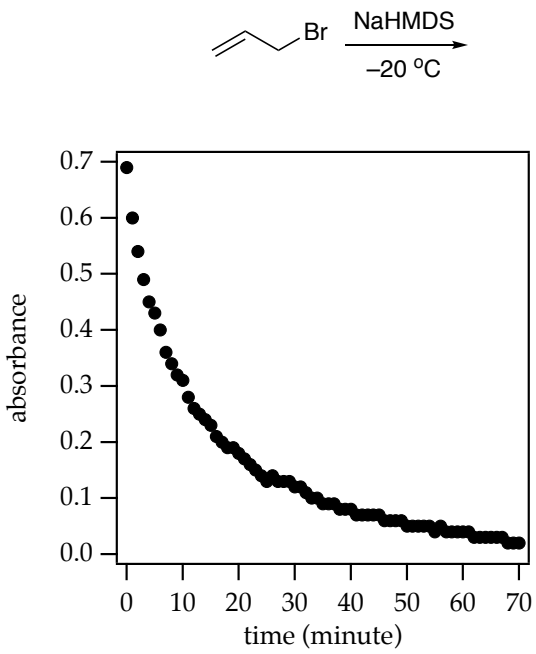


Figure A.2.82. Plot following reaction of 0.20 M NaHMDS and 0.020 M allyl bromide in 0.40 M TMEDA/toluene recorded at –20 °C at 1 spectrum per minute. NaHMDS reacts with allyl bromide, making it difficult to study the allylation of mixed dimer **7**.

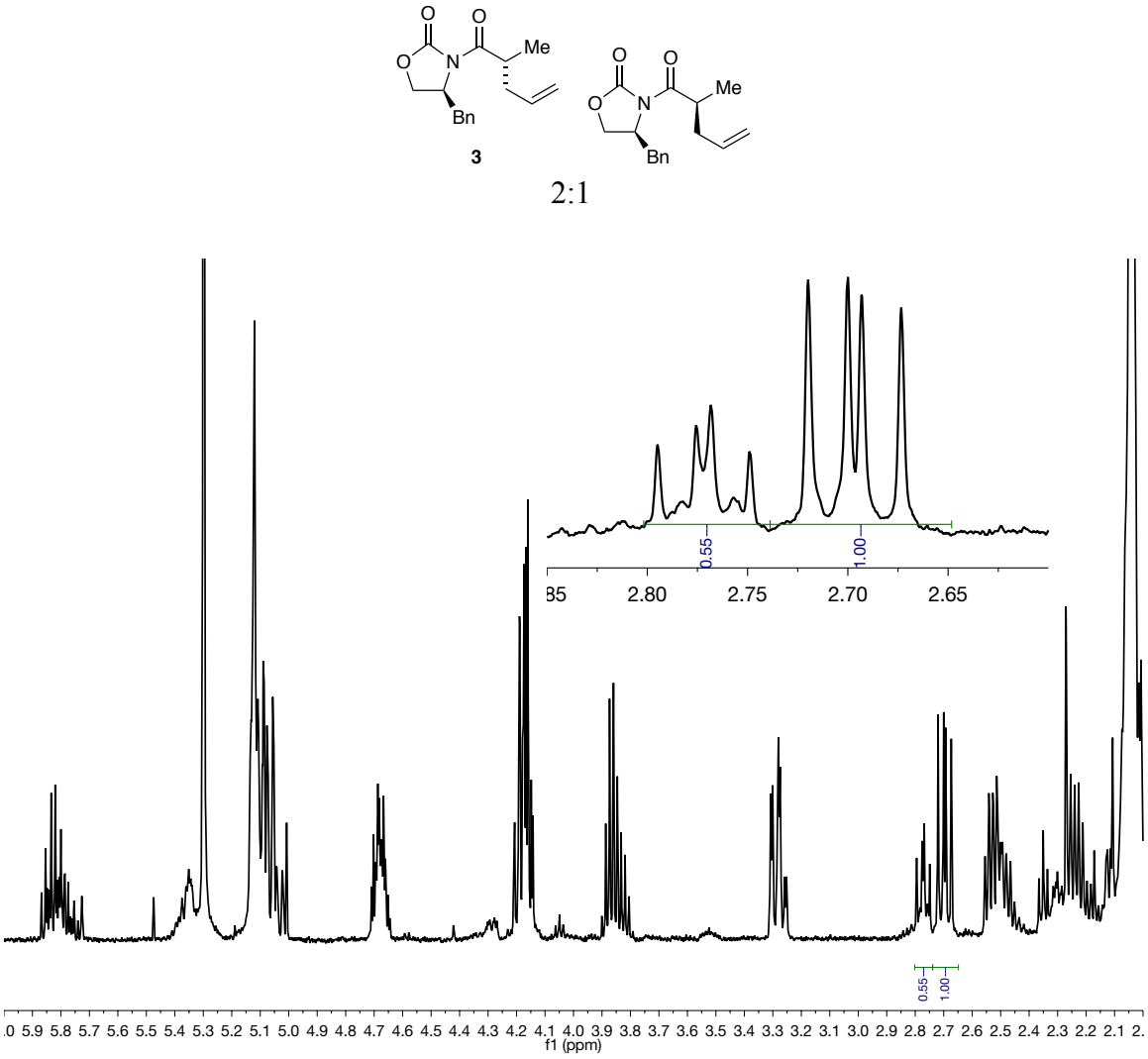


Figure A.2.83. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of **3** prepared from **6**. The integration provides a selectivity of 2:1, significantly lower than the allylation of monomer **4**.

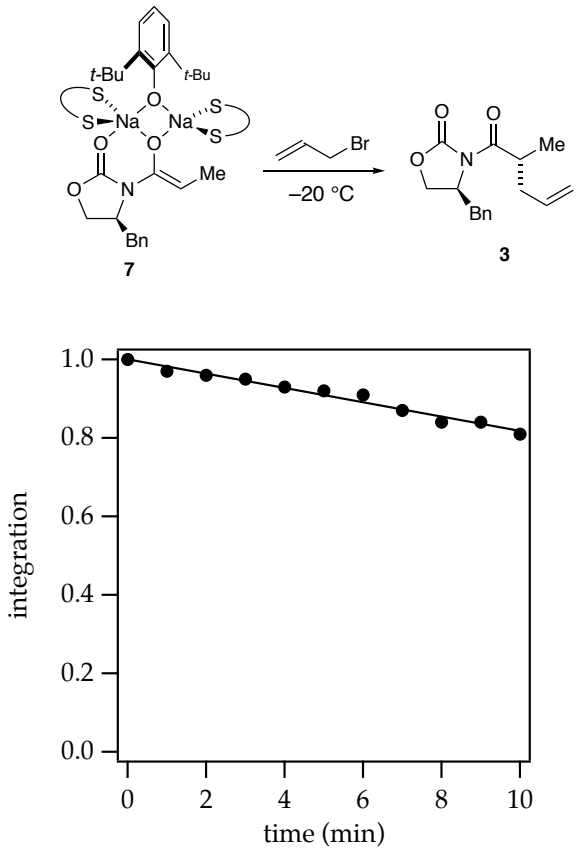


Figure A.2.84. Plot following reaction of 0.40 M NaHMDS, 0.20 M **7**, and 0.020 M allyl bromide in 0.80 M TMEDA/toluene recorded at –20 °C at 1 spectrum per minute. k_{obsd} = 0.0183 ± 0.0009. k_7/k_4 = 0.81. Allylation of phenolate-derived mixed dimer **7** is slightly slower than the allylation of monomer **4**.

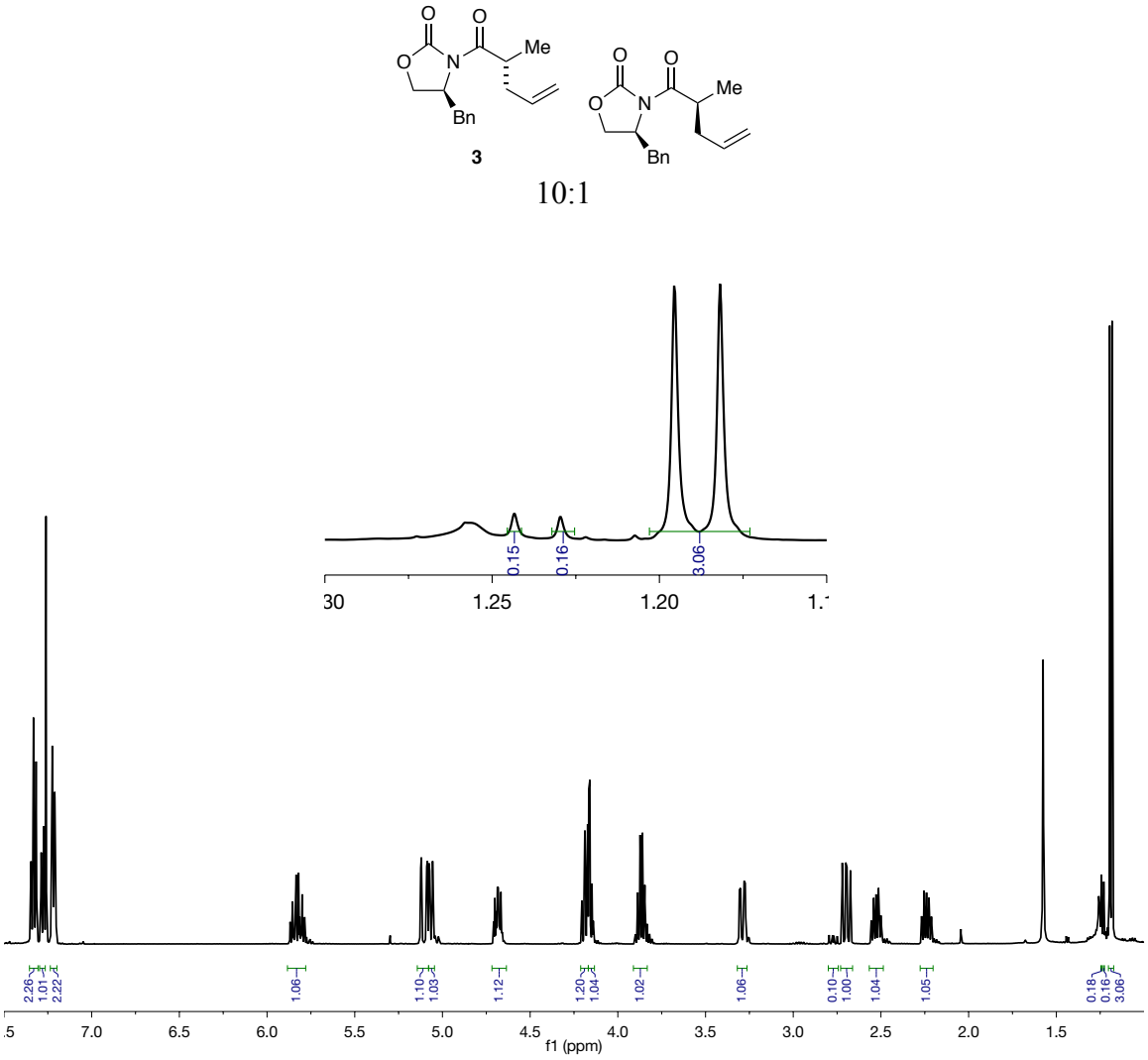


Figure A.2.85. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **3** prepared from **7** in $CDCl_3$ recorded at rt. An isolated yield of 86% was obtained. The integration provides a selectivity of 10:1, lower than the monomer reaction.

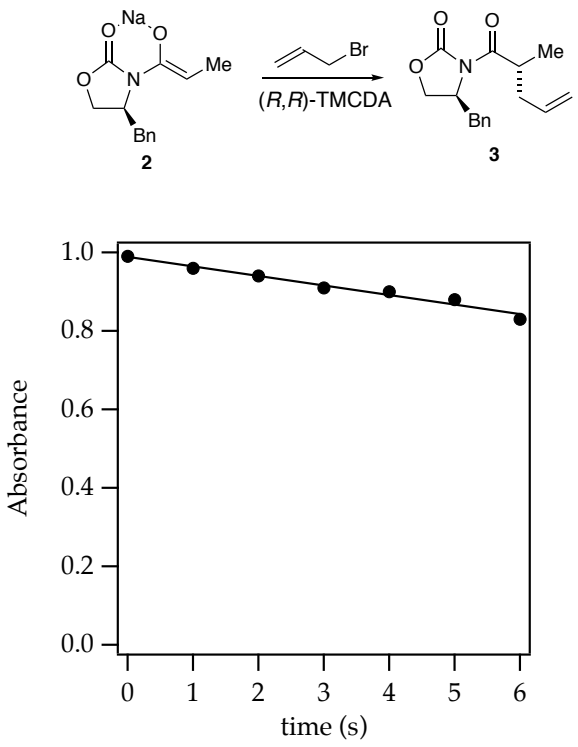


Figure A.2.86. Plot following reaction of 0.20 M (*S*)-**2** and 0.020 M allyl bromide in 0.40 M (*R,R*)-TMCDA in toluene recorded at –20 °C at 1 spectrum per minute. k_{obsd} = 0.024 ± 0.002. $k_{(R,R)\text{-TMCDA}}/k_{TMEDA}$ = 1.1.

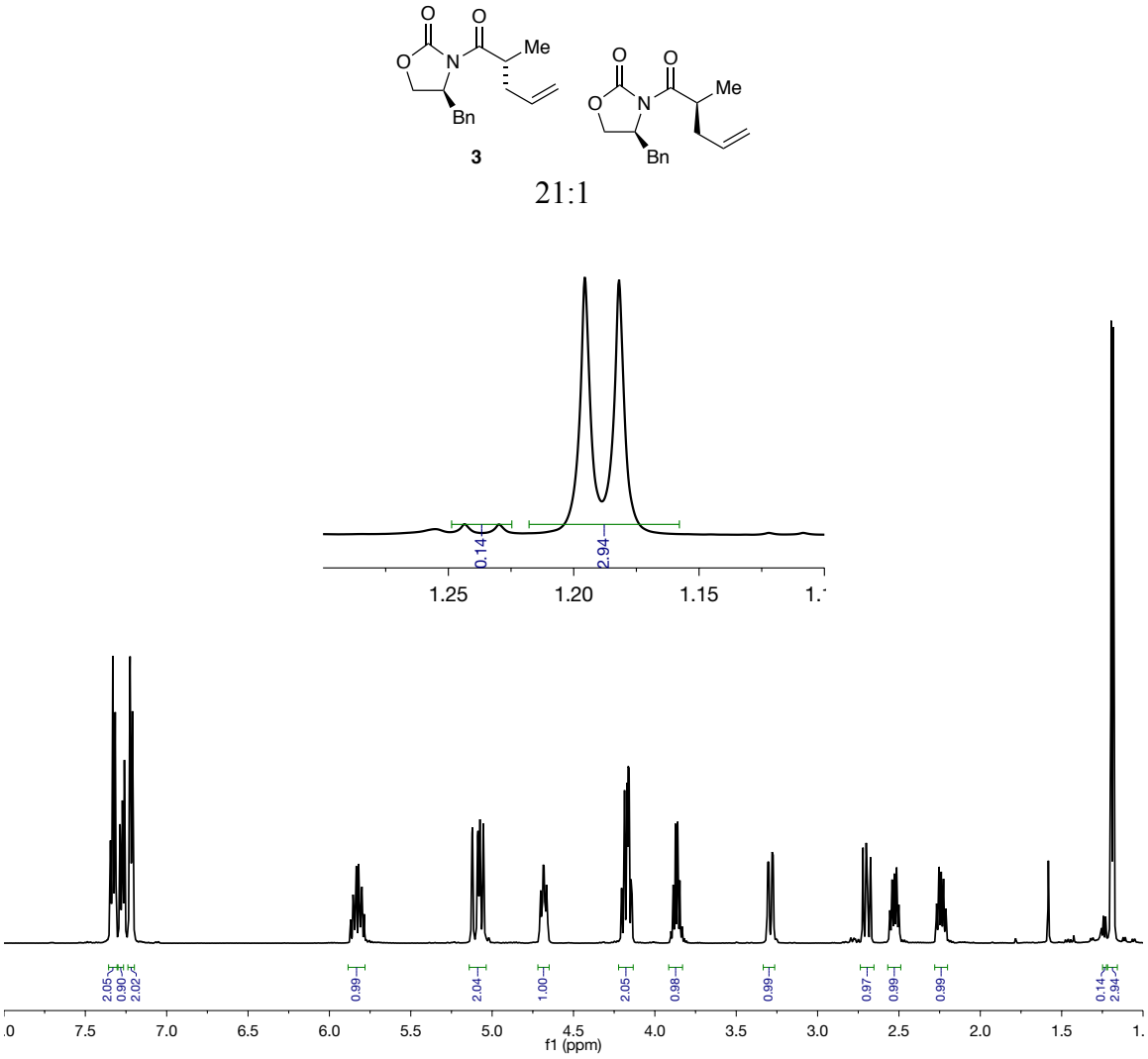


Figure A.2.87. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **3** prepared from **4** in (*R,R*)-TMCDA. An isolated yield of 87% was obtained. The integration provides a selectivity of 21:1, indistinguishable from that obtained from monomer **4**.

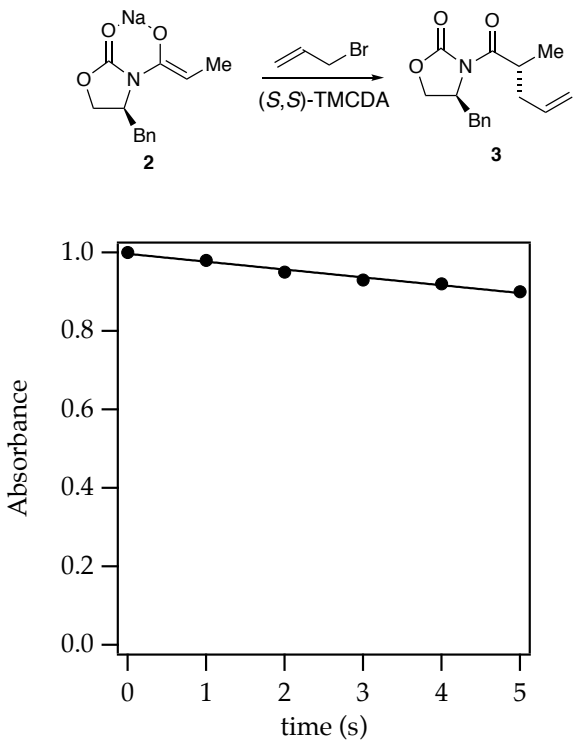


Figure A.2.88. Plot following reaction of 0.20 M (*S*)-**2** and 0.020 M allyl bromide in 0.40 M (*S,S*)-TMCDA in toluene recorded at –20 °C at 1 spectrum per minute. $k_{obsd} = 0.020 \pm 0.001$. $k_{(S,S)\text{-TMCDA}}/k_{TMEDA} = 0.9$.

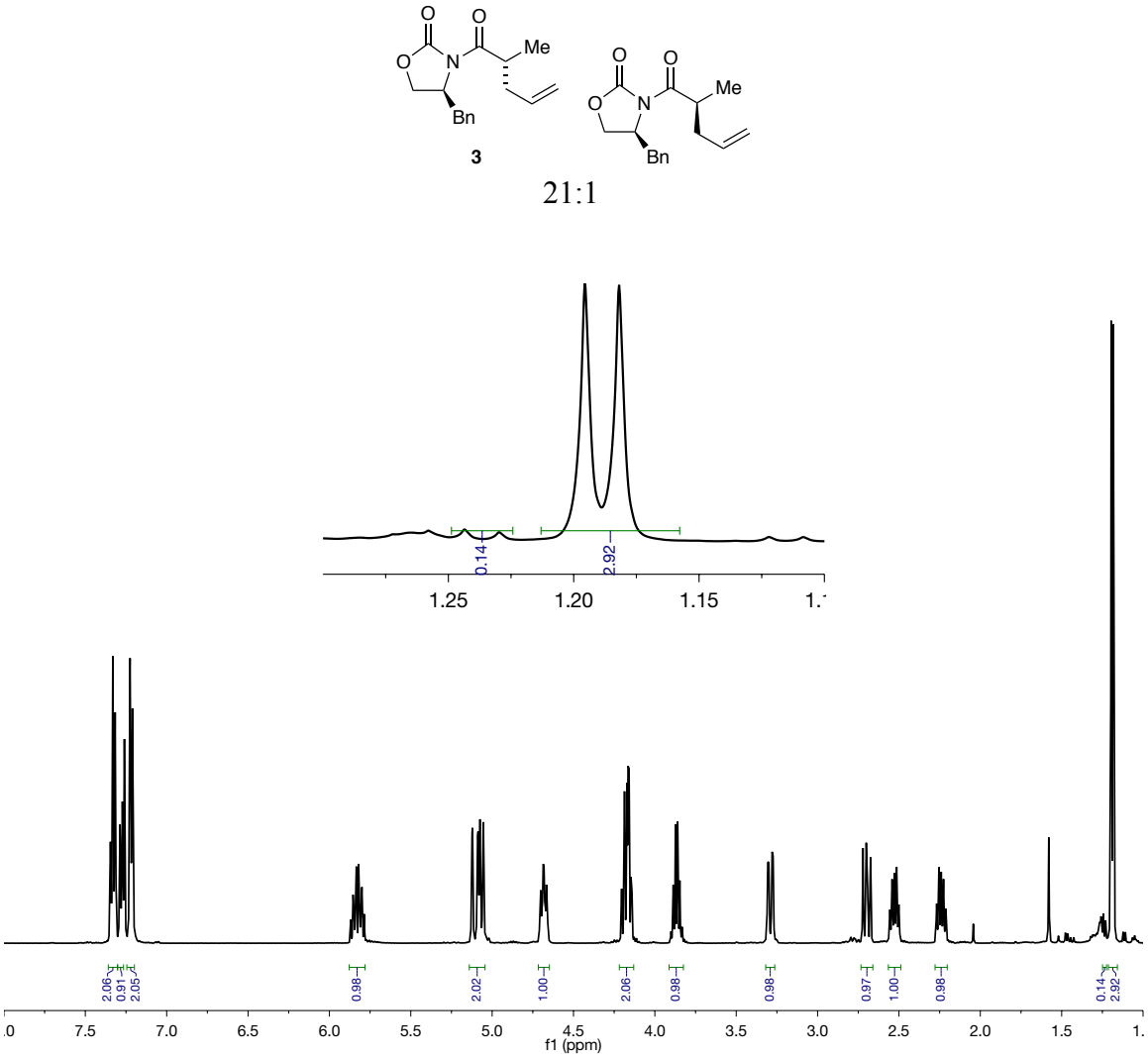


Figure A.2.89. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **3** prepared from **4** in (*S,S*)-TMCDA. An isolated yield of 90% was obtained. The integration provides a selectivity of 21:1, which is the same as that obtained from monomer **4**.

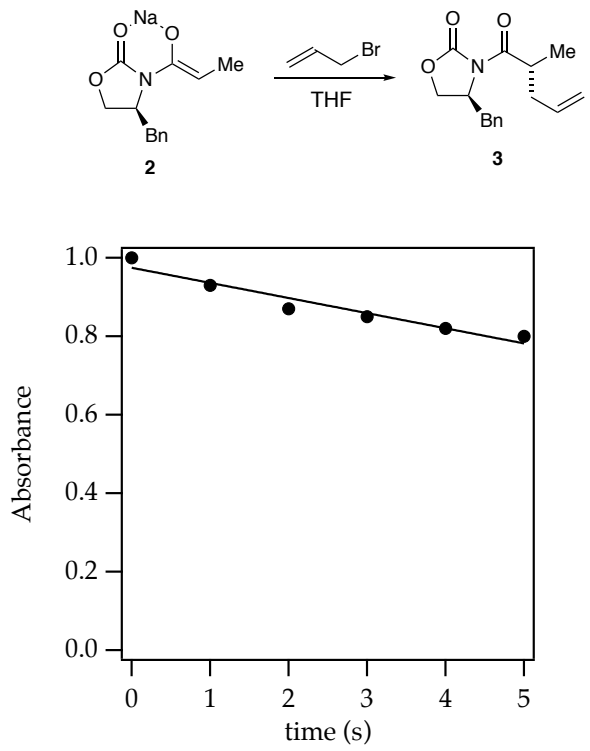


Figure A.2.90. Plot following reaction of 0.20 M NaHMDS, 0.20 M **1** and 0.020 M allyl bromide in THF recorded at –20 °C at 1 spectrum per minute. k_{obsd} = 0.0396 ± 0.005. The allylation in THF is slightly faster than in TMEDA (k_{THF}/k_{TMEDA} = 1.7).

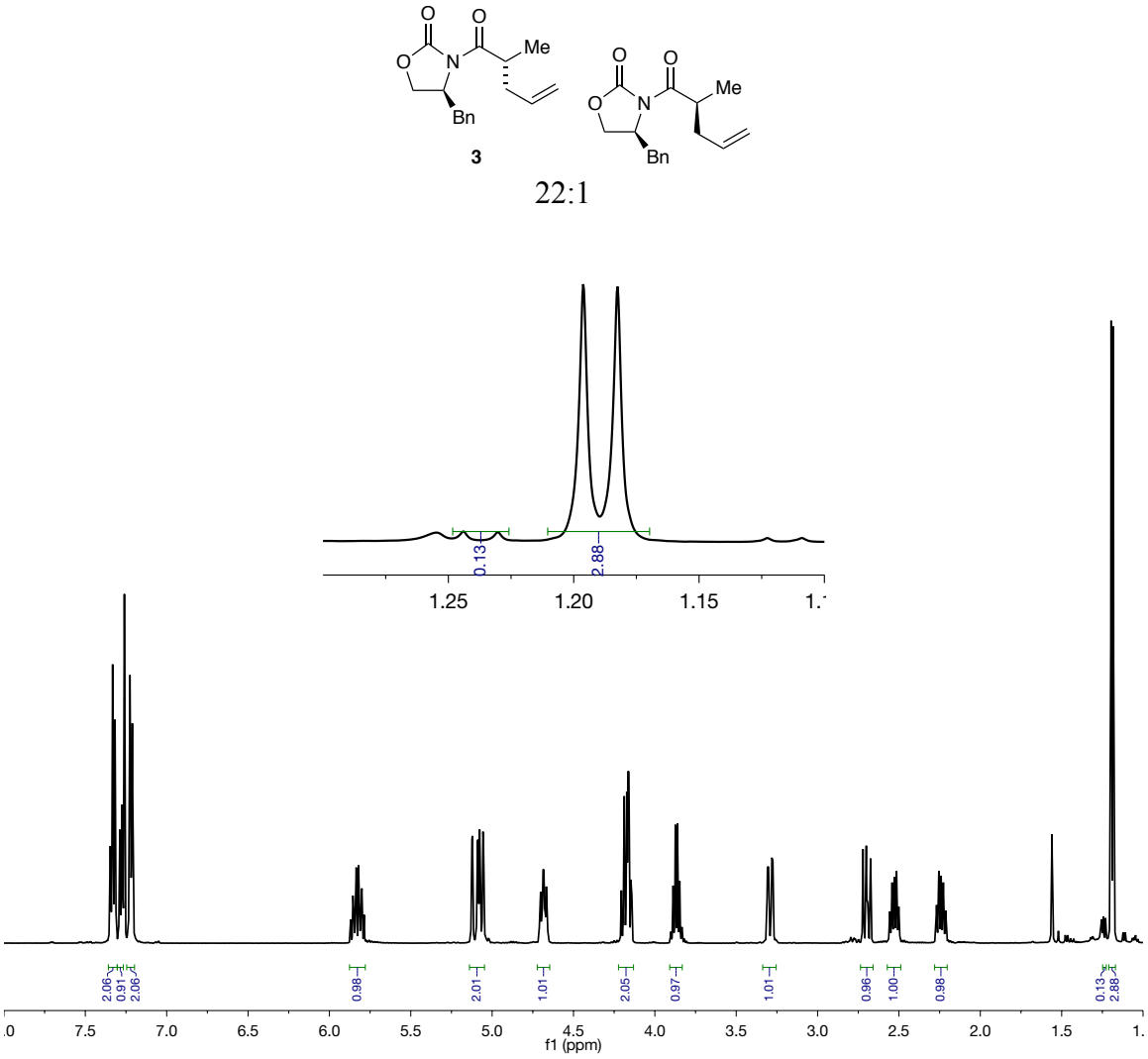


Figure A.2.91. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **3** prepared from (*S*)-**2** in THF An isolated yield of 83% was obtained. The integration provides a selectivity of 22:1, same as the monomer reaction.

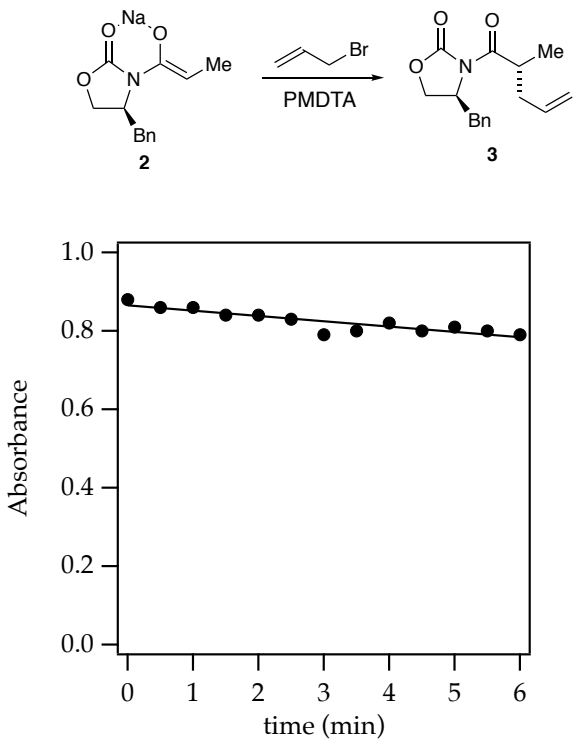


Figure A.2.92. Plot following reaction of 0.10 M **2** and 0.10 M allyl bromide in 0.20 M PMDTA recorded at –20 °C at 1 spectrum per minute. k_{obsd} = 0.0135 ± 0.002. The allylation in PMDTA is slightly faster than in TMEDA (k_{PMDTA}/k_{TMEDA} = 1.3).

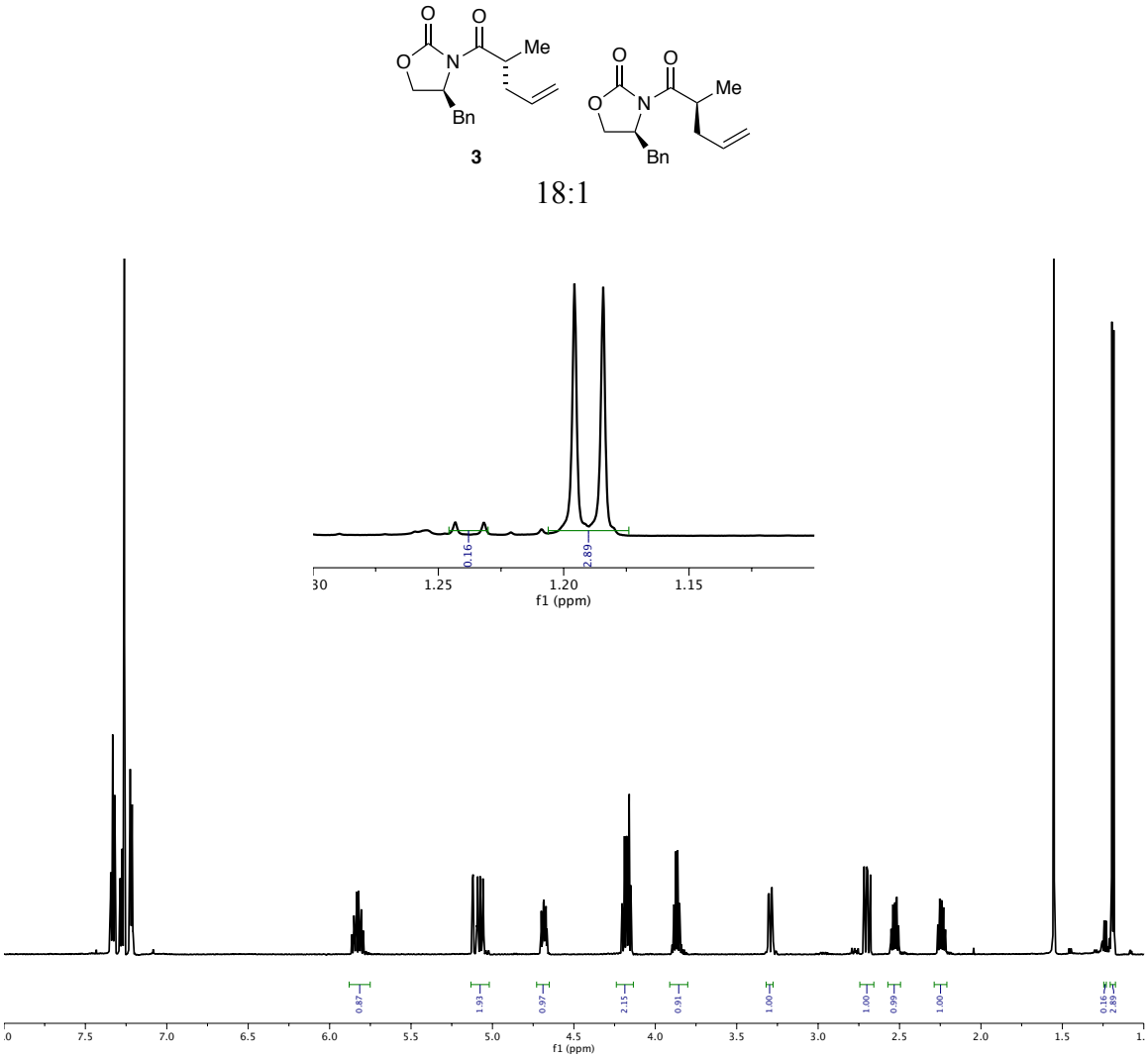


Figure A.2.93. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **3** prepared from (*S*)-**2** in PMDTA An isolated yield of 92% was obtained. The integration provides a selectivity of 18:1.

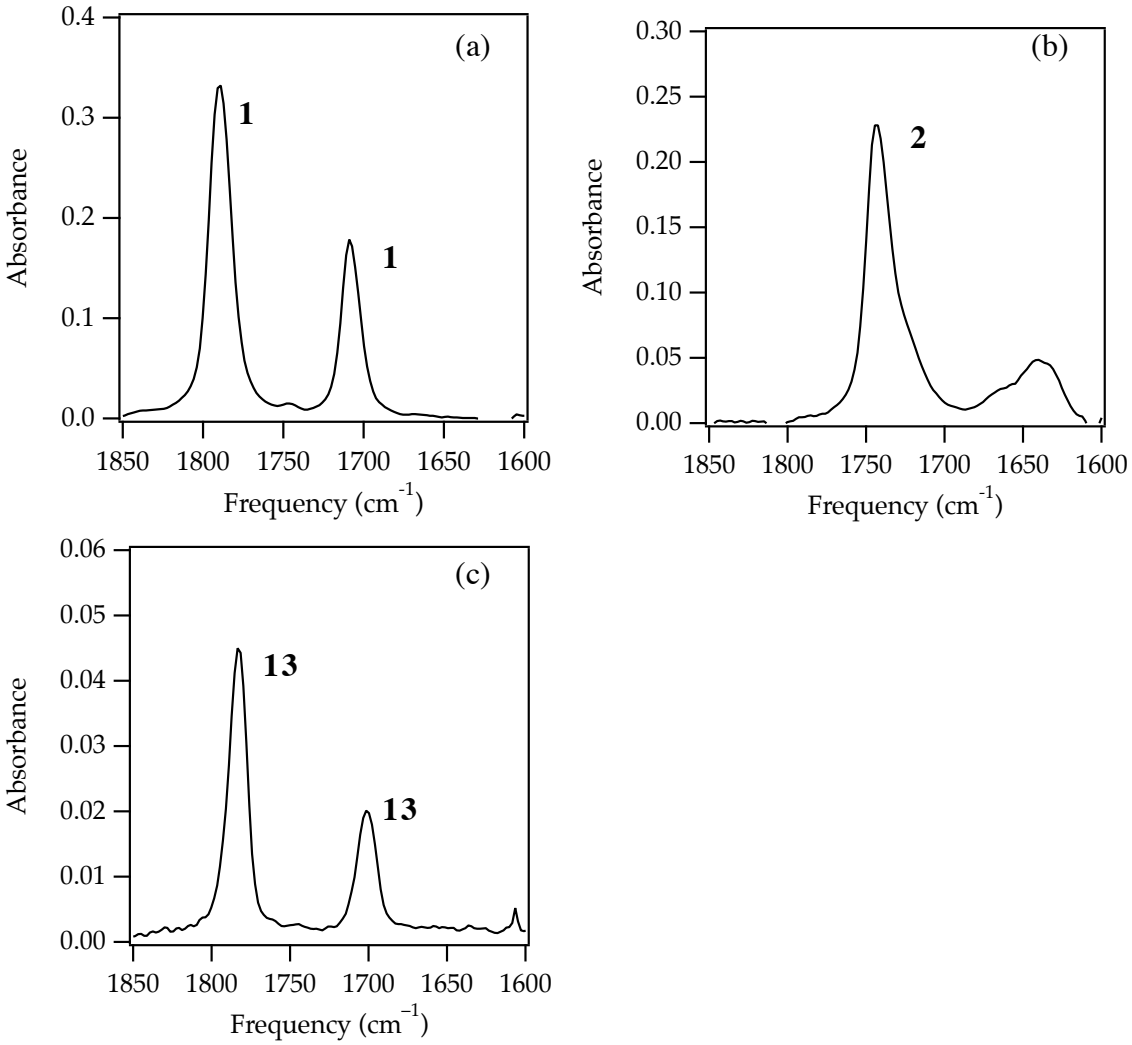


Figure A.2.94. IR spectra of (a) 0.10 M **1** in toluene; (b) 0.10 M **2** in 1.0 M TMEDA/toluene; (c) 0.010 M **13** in toluene recorded at –78 °C.

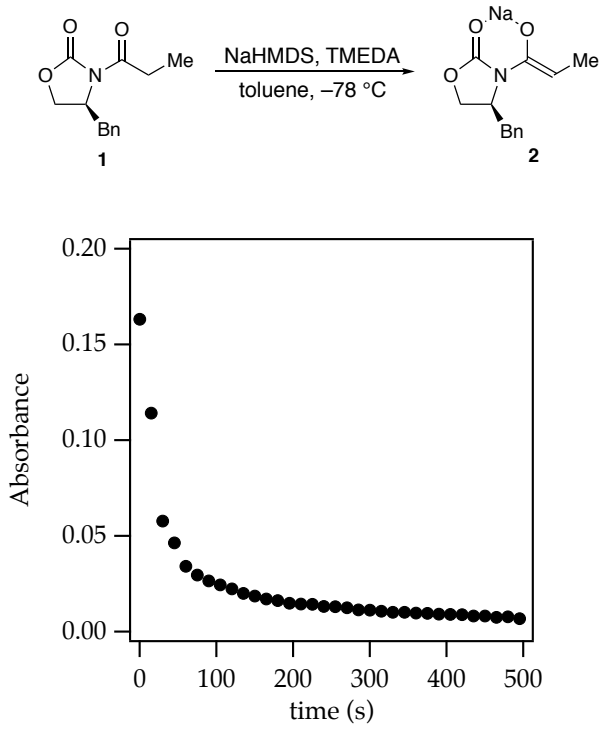


Figure A.2.95. IR spectrum following loss of **1** in a solution of 0.10 M **1** and 0.11 M NaHMDS in 1.0 M TMEDA/toluene recorded at –78 °C.
Enolization of **1** is fast even at stoichiometric condition at low temperature.

(4S)- 4-benzyl-3-((2R)-2-methyl-3-phenylpropanoyl)-2-oxazolidinone (**13**). To a solution of NaHMDS (3.3 mmol, 605 mg) and TMEDA (6.6 mmol, 988 μL) in 5.0 mL toluene under argon at –78 °C was added **1** (3.0 mmol, 699 mg) in 1.0 mL of toluene. The reaction was stirred for 30 minutes, charged with benzyl bromide (20 mmol, 2.4 mL), warmed to 0 °C, and stirred for 0.5 h. The reaction was quenched with 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 20% ethyl acetate in hexanes afforded 825 mg of **13** (85% combined yield) displaying spectroscopic properties described previously. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 2H), 7.29 – 7.27 (m, 2H), 7.26 – 7.25 (m, 3H), 7.23 – 7.17 (m, 1H), 7.08 – 7.03 (m, 2H), 4.67 (ddt, *J* = 9.3, 7.9, 3.2 Hz, 1H), 4.20 – 4.08 (m, 3H), 3.15 (dd, *J* = 13.2, 7.3 Hz, 1H), 3.07 (dd, *J* = 13.5, 3.4 Hz, 1H), 2.68 (dd, *J* = 13.3, 7.6 Hz, 1H), 2.55 (dd, *J* = 13.5, 9.3 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.56, 153.05, 139.18, 135.17, 129.39, 129.37, 128.90, 128.34, 127.28, 126.41, 65.89, 55.10, 39.91, 39.57, 37.71, 16.76.

Schmidt, B.; Wildemann, H. *J. Chem. Soc., Perkin Trans. 1,* **2002**, 1050.

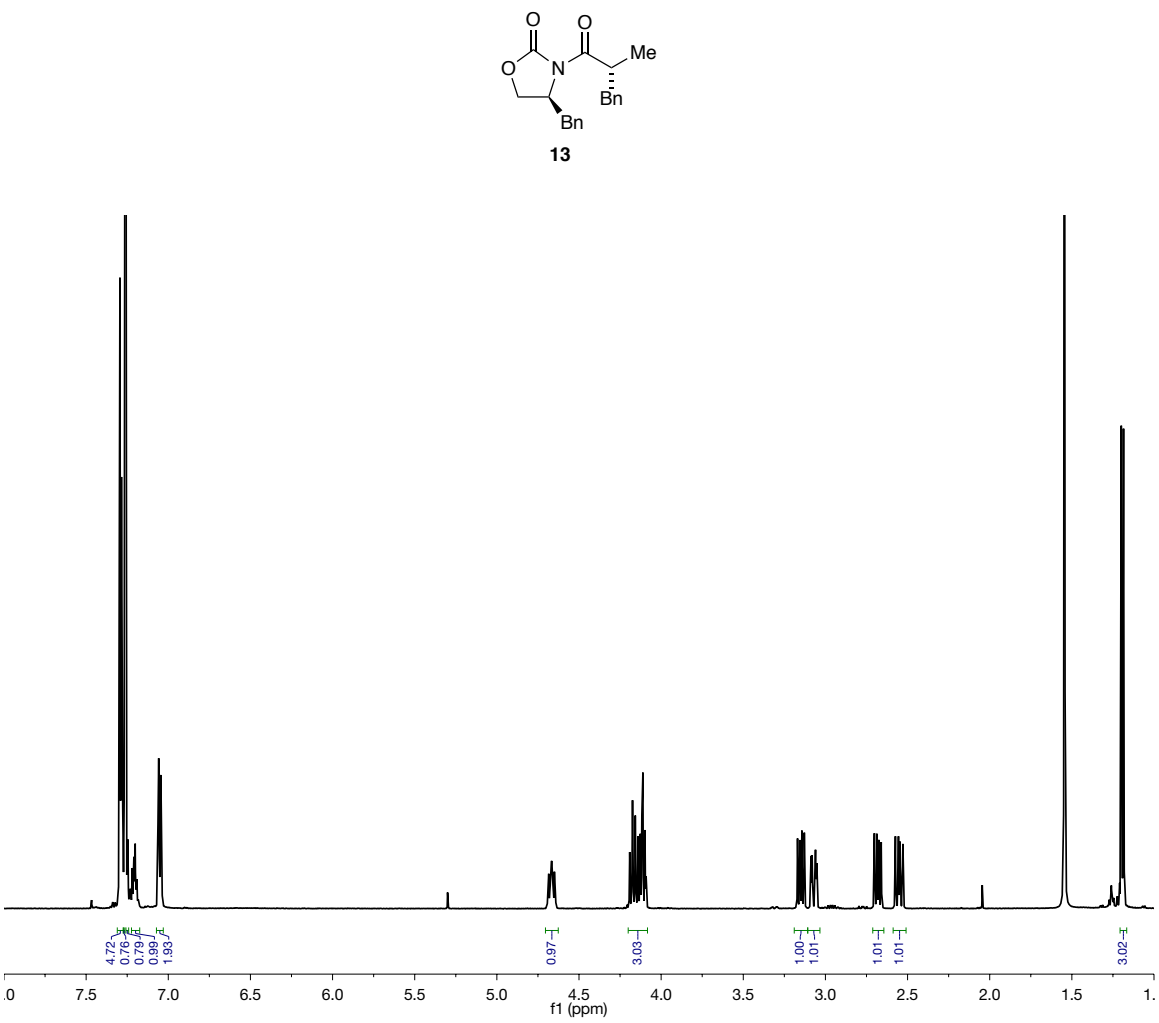


Figure A.2.96. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **13**.

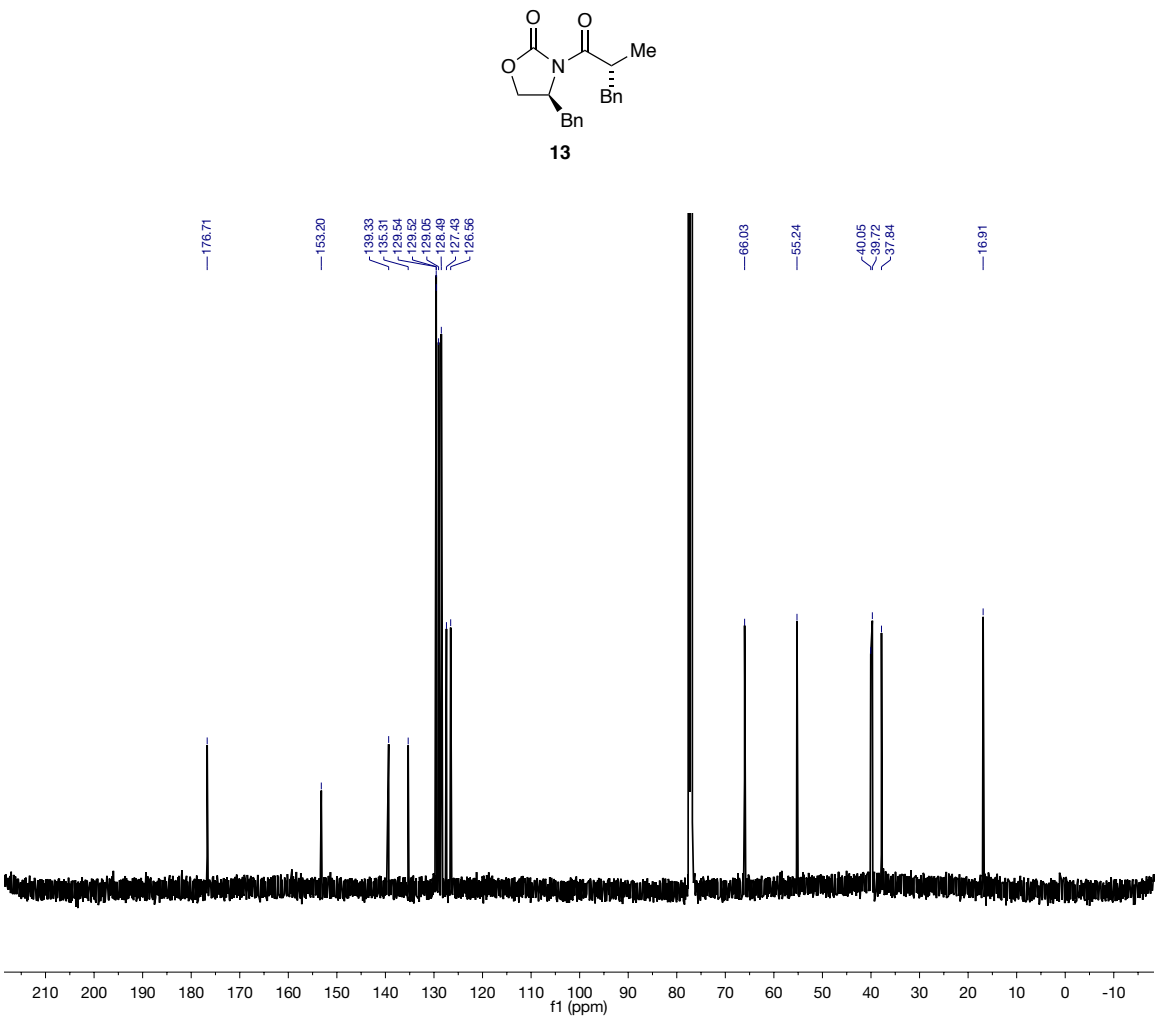


Figure A.2.97. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **13**.

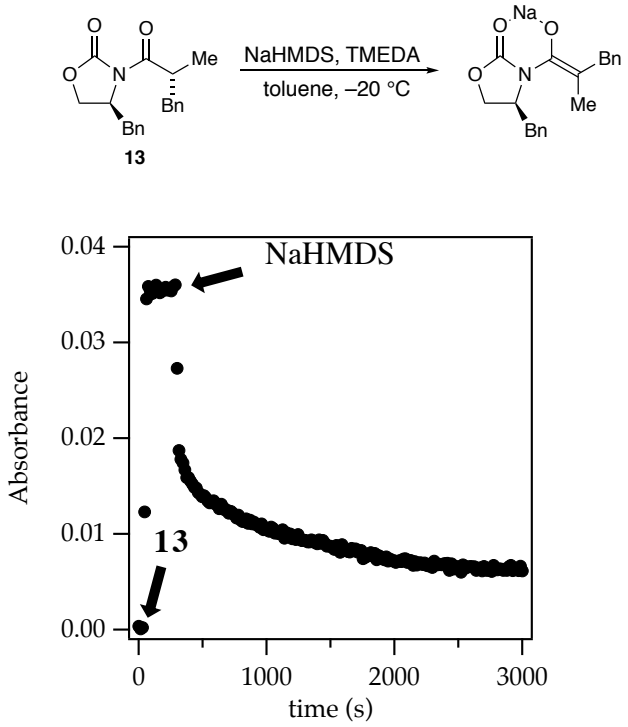


Figure A.2.98. IR spectrum following loss of **13** in a solution of 0.010 M **13** and 0.015 M NaHMDS in 0.030 M TMEDA/toluene recorded at –20 °C.
The enolization is much slower than for non-branched enolates, demanding a higher reaction temperature which results in some deacylation.

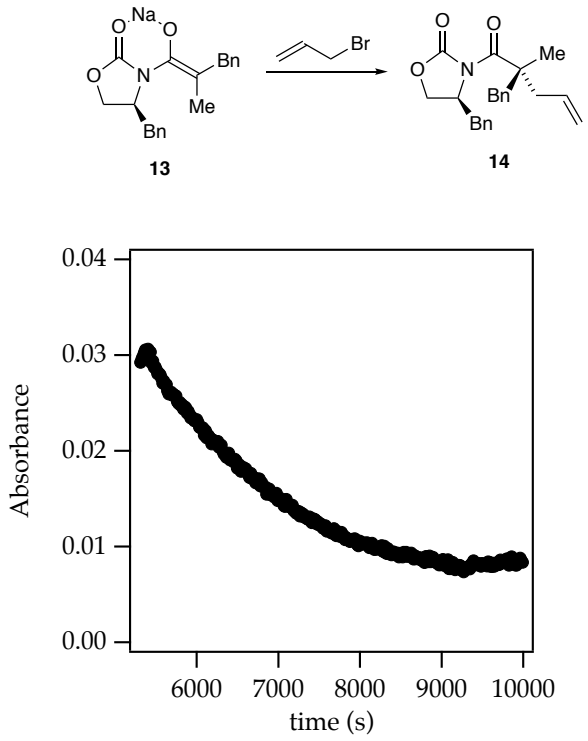


Figure A.2.99. IR spectrum following loss of enolate **13** in a solution of 0.010 M **13**, 0.0050 M NaHMDS and 0.10 M allylbromide in 0.030 M TMEDA/toluene recorded from –20 °C to rt. The spectroscopy is often capricious owing to precipitation of NaBr disturbing the absorbance.

(*S*)-4-benzyl-3-((*S*)-2-benzyl-2-methylpent-4-enoyl)oxazolidin-2-one (**14**). To a solution of NaHMDS (0.10 mmol, 18.3 mg) and TMEDA (0.20 mmol, 30 μL) in toluene (2.0 mL) under argon was added **13** (0.070 mmol, 22.6 mg) in 0.10 mL of toluene. Reaction was stirred under argon for 1 hr at –20 °C. Allyl bromide (0.40 mmol, 35 μL) was injected, and the mixture was warmed to 0 °C over 2 hr. The reaction was quenched with 3.0 mL of saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 15% ethyl acetate in hexanes afforded 13.7 mg of product (54% combined yield) shown to be an 11:1 mixture of **14** and its minor diastereomer. ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 7.23 – 7.19 (m, 5H), 5.77 (dddd, *J* = 16.9, 10.1, 8.0, 6.7 Hz, 1H), 5.11 (dq, *J* = 17.0, 1.6 Hz, 1H), 5.06 (ddt, *J* = 10.0, 2.0, 1.0 Hz, 1H), 4.61 (ddt, *J* = 10.7, 6.7, 3.3 Hz, 1H), 4.15 – 4.10 (m, 2H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.18 (dd, *J* = 13.2, 3.3 Hz, 1H), 3.12 – 3.04 (m, 2H), 2.61 (dd, *J* = 13.2, 10.6 Hz, 1H), 2.29 (ddt, *J* = 14.3, 6.7, 1.4 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.07, 152.77, 137.72, 135.94, 134.39, 130.58, 129.54, 129.06, 128.20, 127.38, 126.74, 118.27, 66.43, 58.32, 50.54, 42.01, 40.73, 38.01, 23.38. m/z calculated for $(M+H)^+$ 364.19072, found 364.19097.

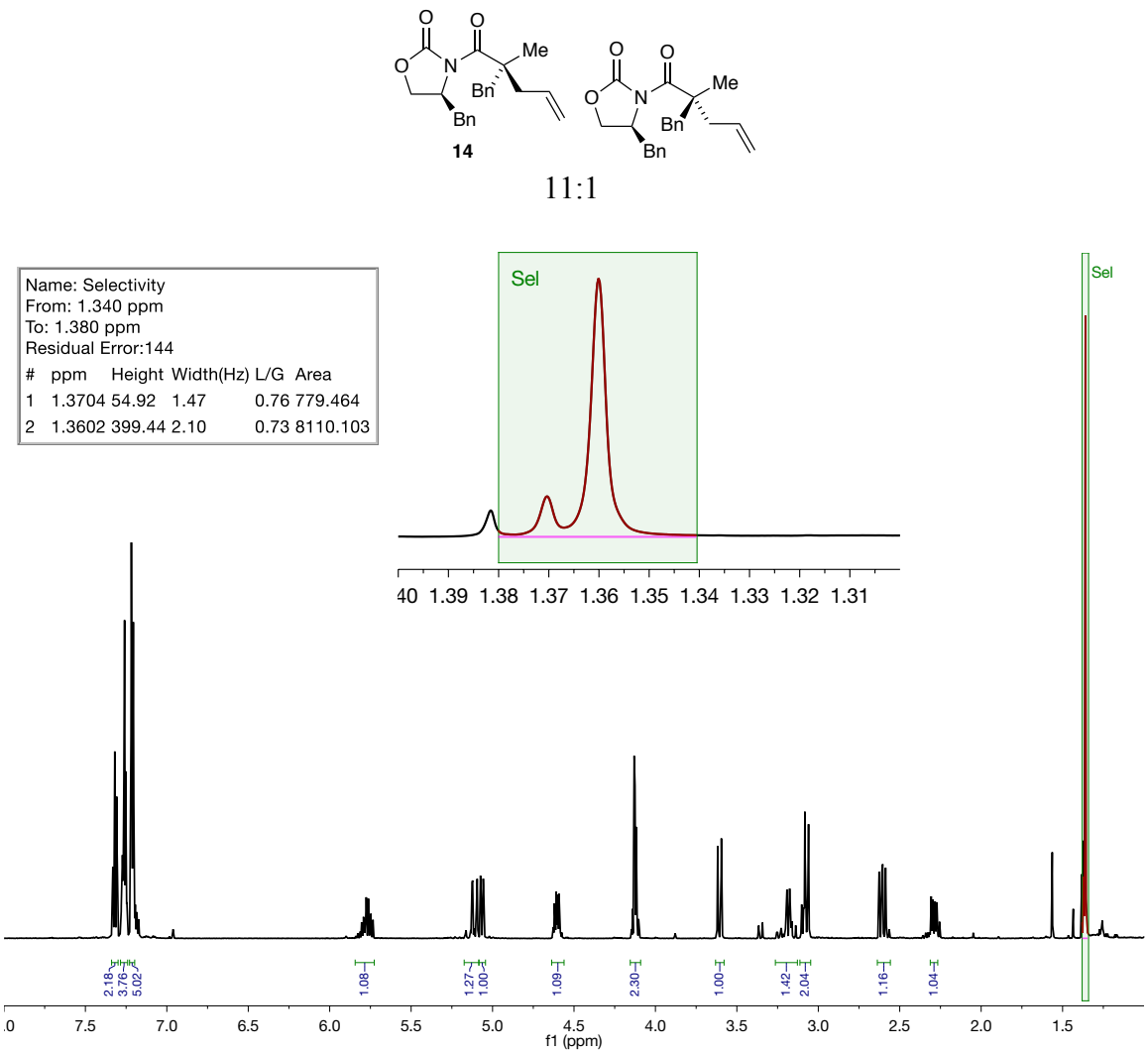


Figure A.2.100. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14**. An isolated yield of 54% was obtained. The integration shows an 11:1 selectivity.

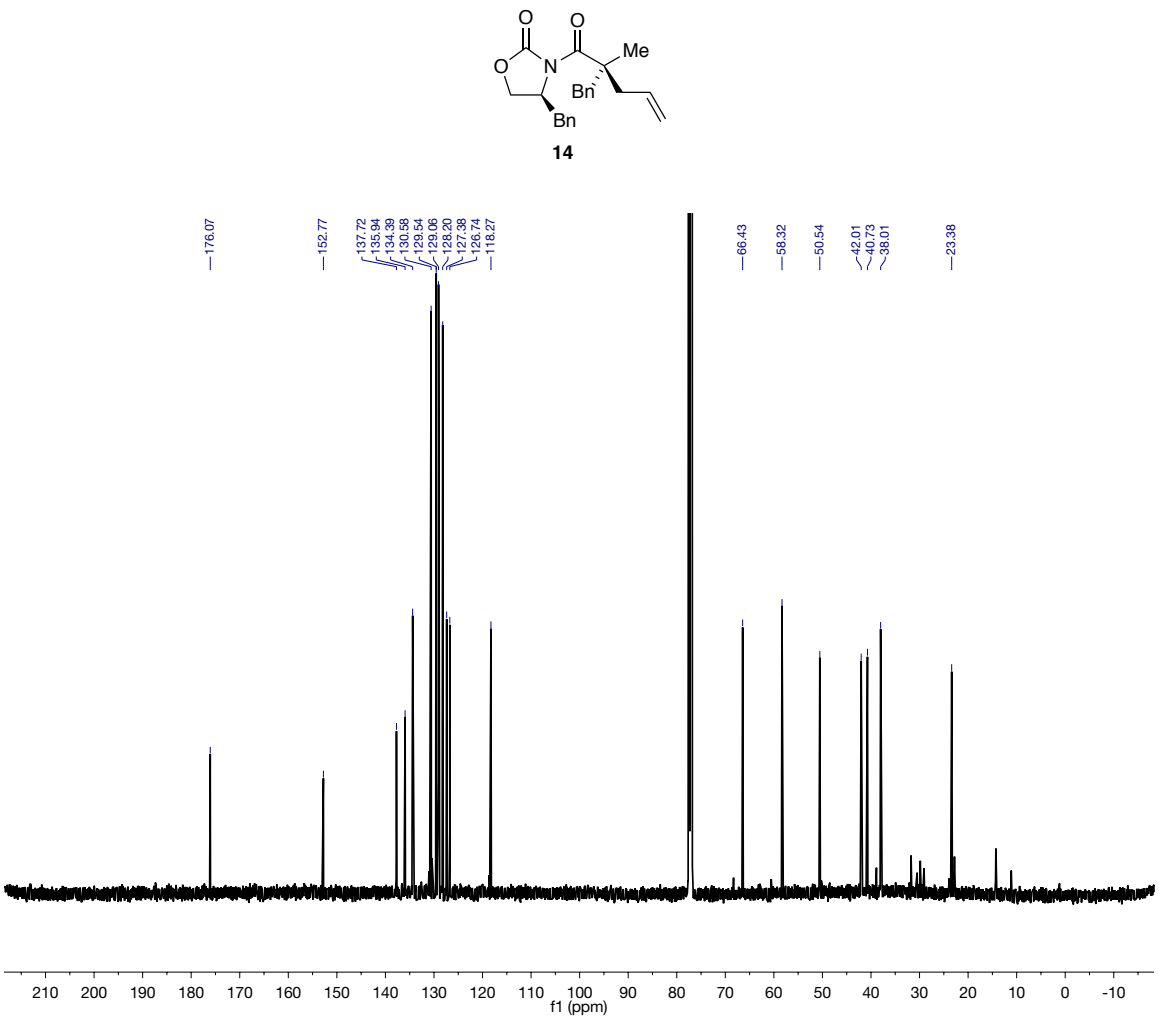


Figure A.2.101. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **14** in $CDCl_3$.

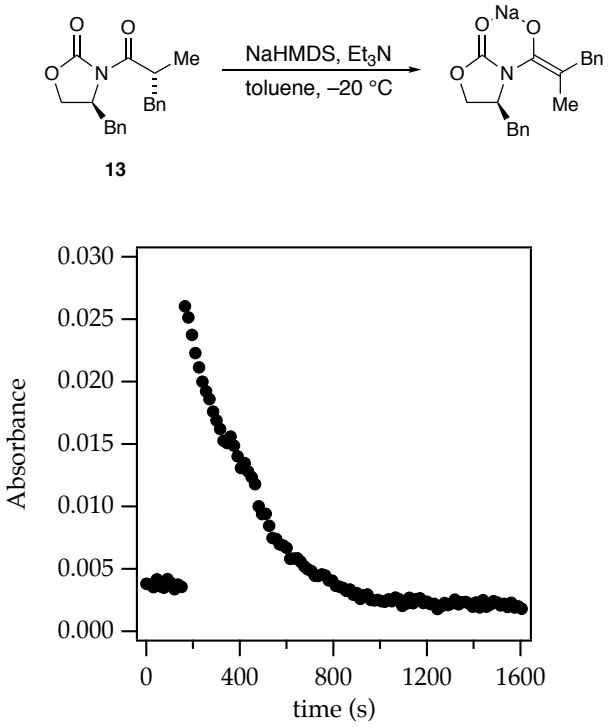
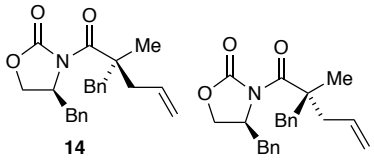


Figure A.2.102. IR spectrum following loss of **13** in a solution of 0.010 M **13** and 0.015 M NaHMDS in 0.10 M Et_3N/toluene recorded at –20 °C. The elevated enolization rate suppresses decomposition. A new species attributed to a **13**/NaHMDS complex is observed at early time in the IR spectrum.



11:1

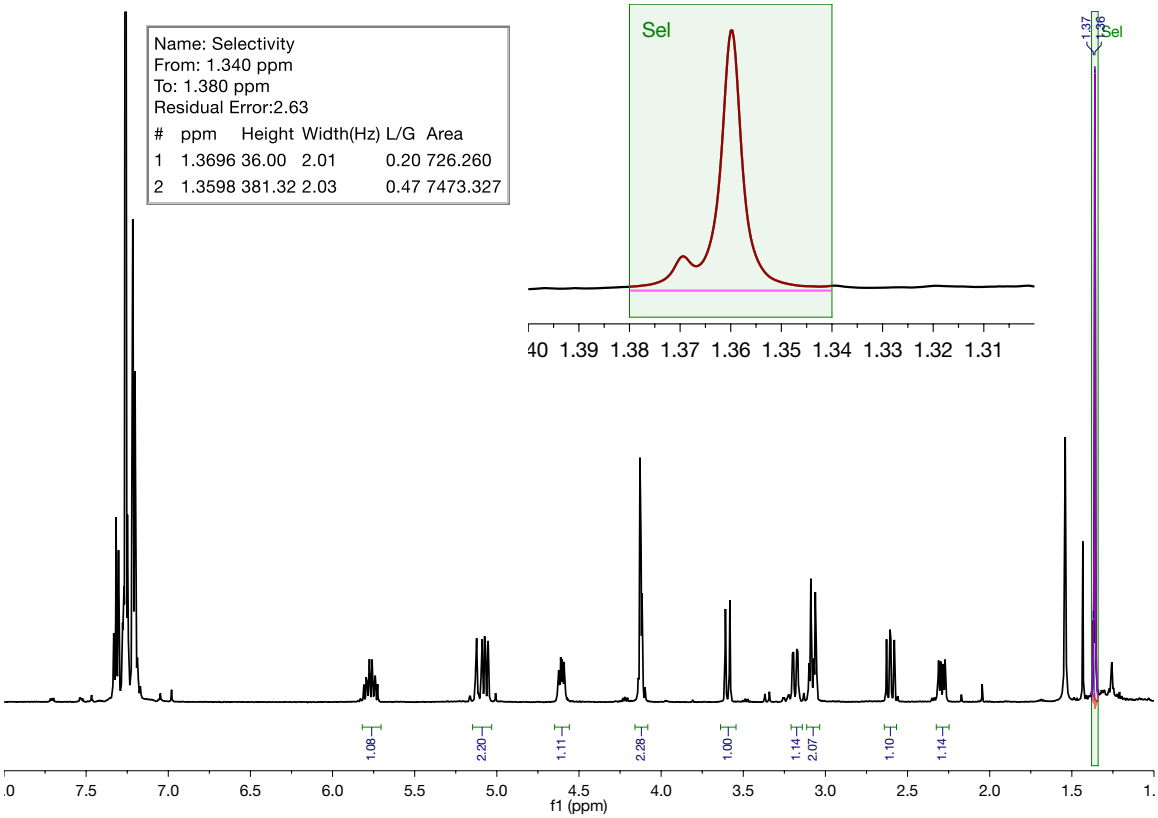


Figure A.2.103. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from Et_3N. An isolated yield of 70%was obtained. The integration shows 11:1 selectivity.

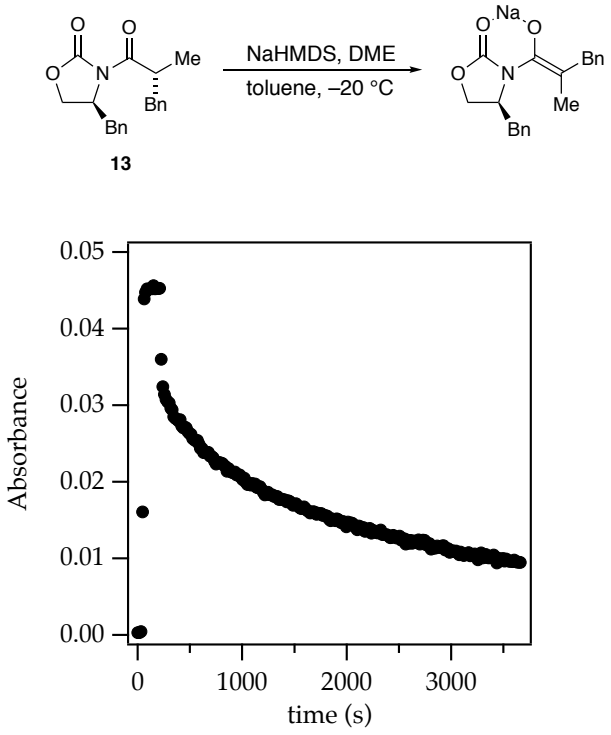
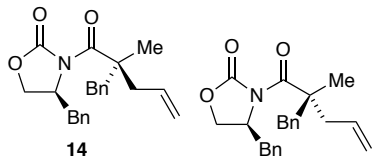


Figure A.2.104. IR spectrum following loss of **13** in a solution of 0.010 M **13** and 0.015 M NaHMDS in 0.040 M DME/toluene recorded at –20 °C. The slower enolization is affiliated with greater decomposition.



11:1

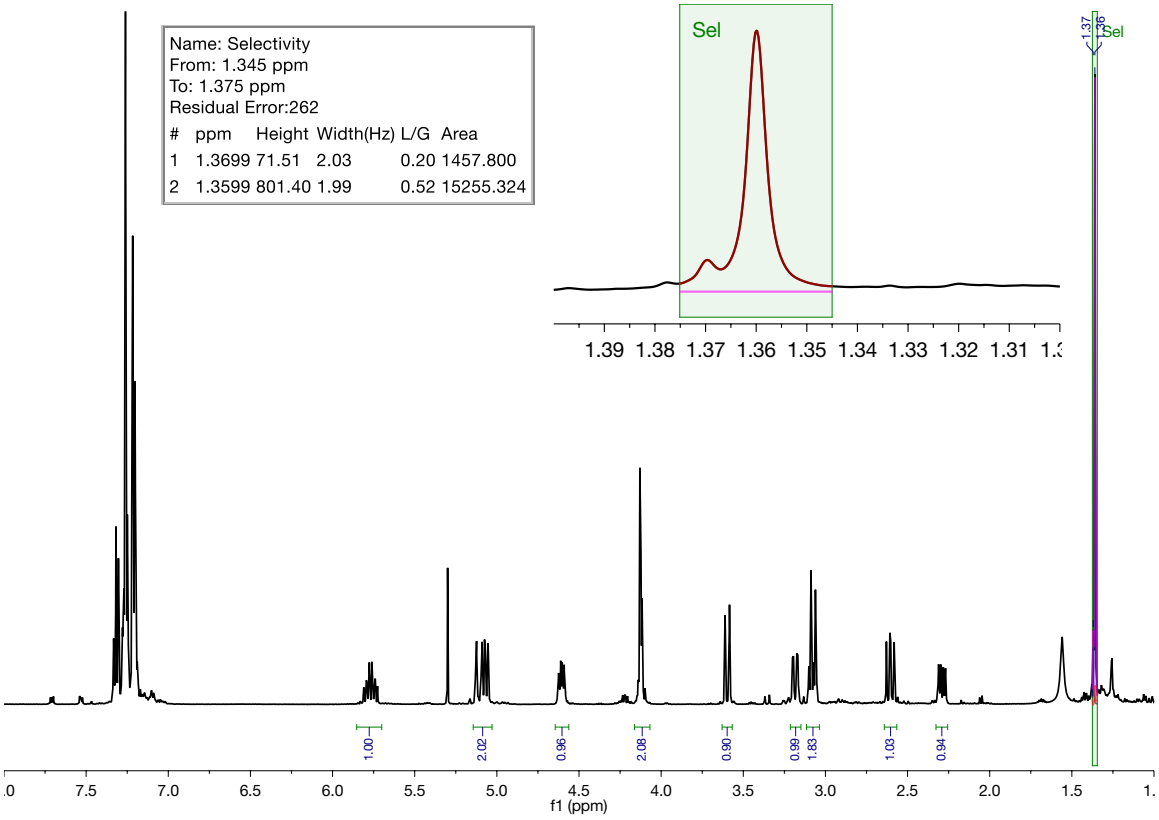
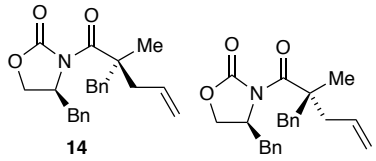


Figure A.2.105. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **13** in DME. An isolated yield of 40% was obtained. The integration shows an 11:1 selectivity.



30:1

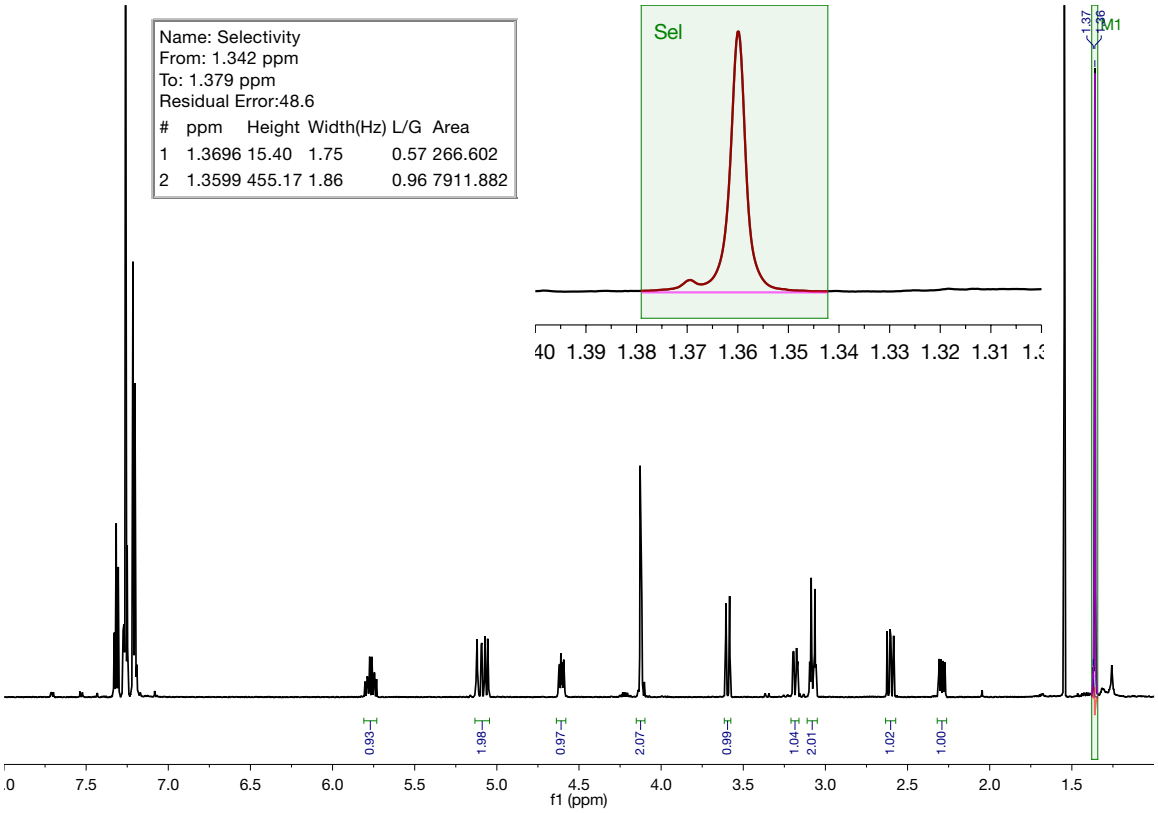


Figure A.2.106. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **13** in (*R,R*)-TMCDA. An isolated yield of 40%was obtained. The integration shows a 30:1 selectivity.

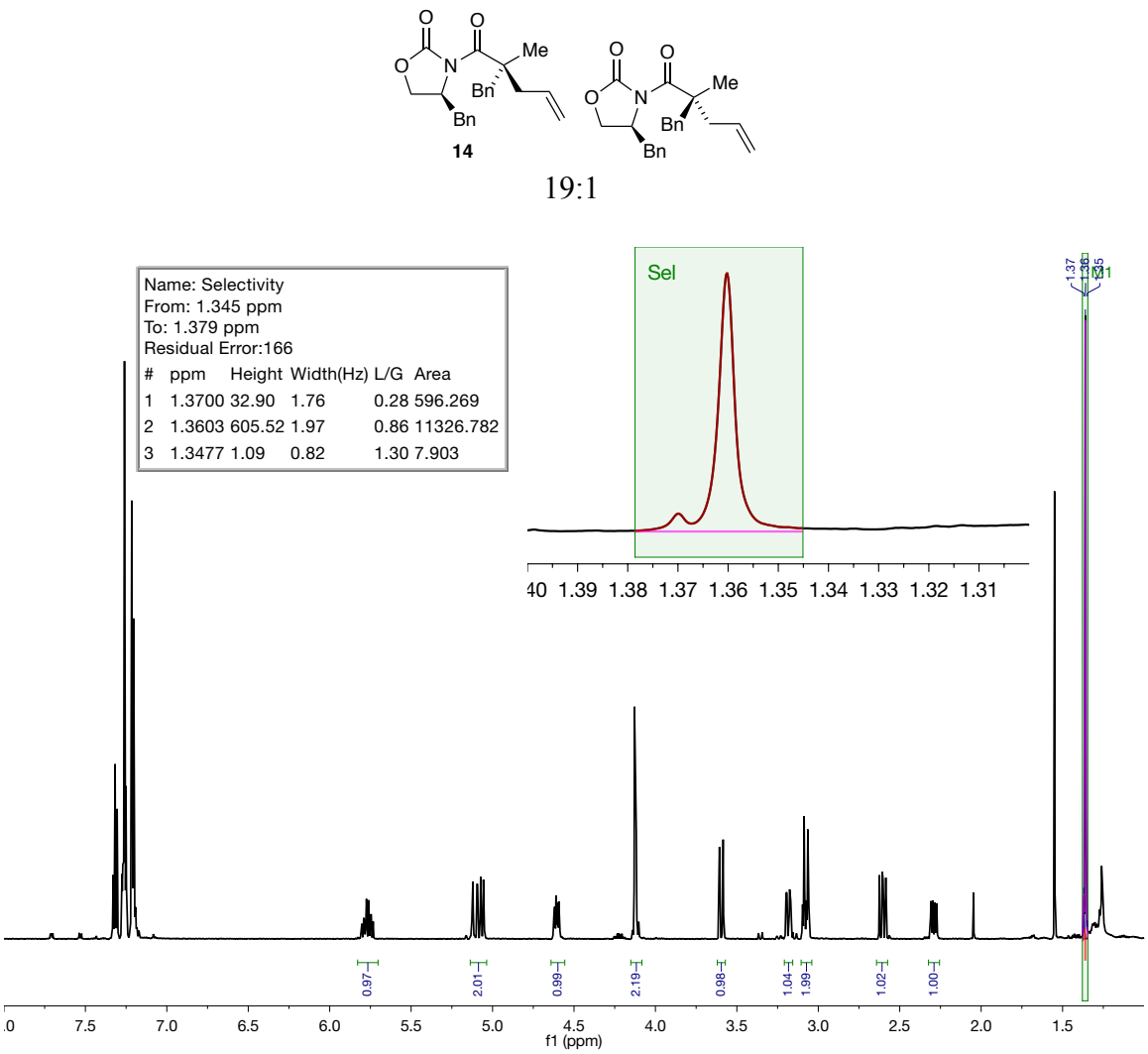


Figure A.2.107. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **13** in (*S,S*)-TMCDA. An isolated yield of 52%was obtained. The integration shows a 19:1 selectivity.

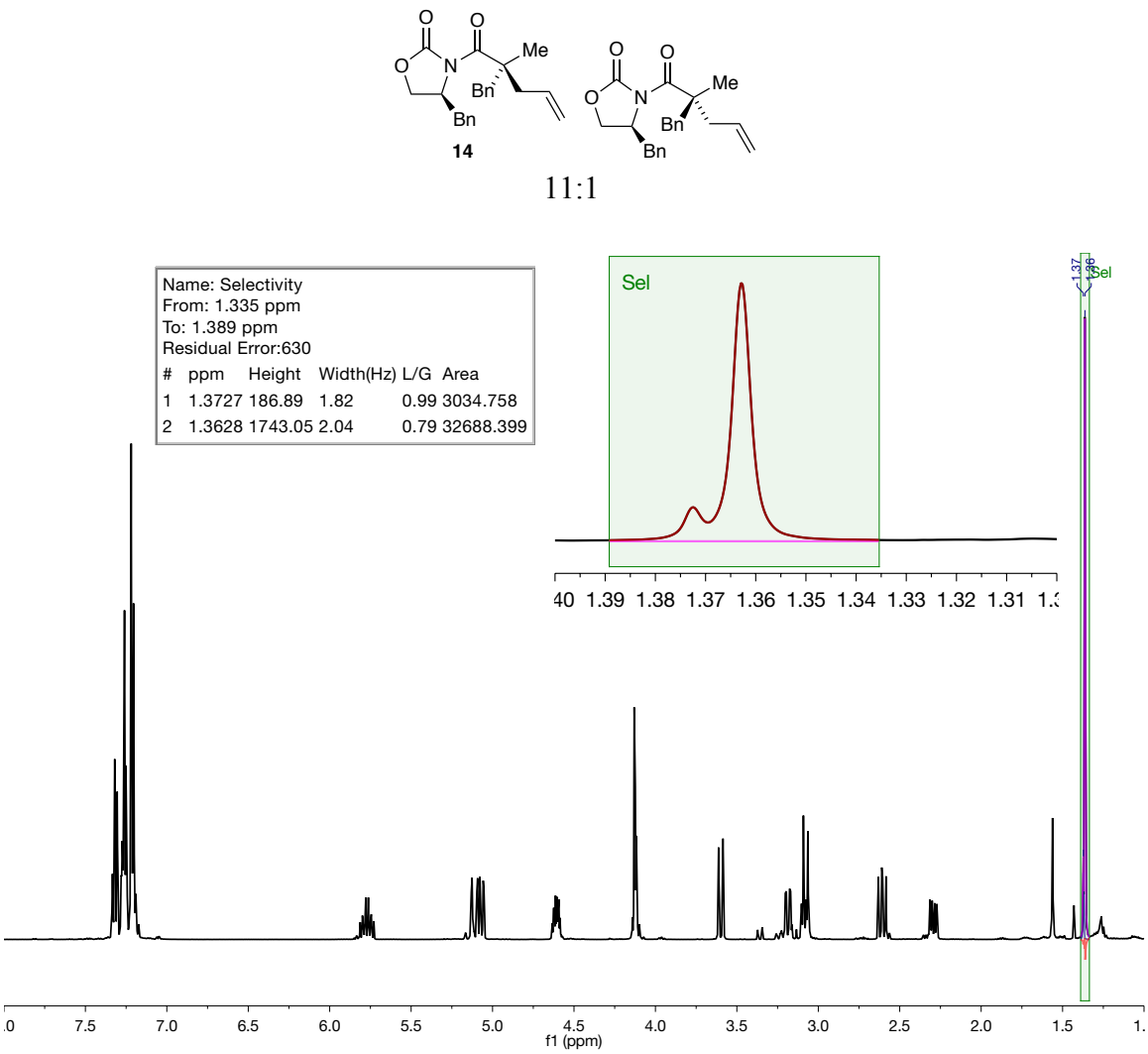


Figure A.2.108. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **13** using Et_3N/toluene for the enolization with addition of (*R,R*)-TMCDA prior to alkylation. An isolated yield of 71%was obtained. The integration shows a 11:1 selectivity.

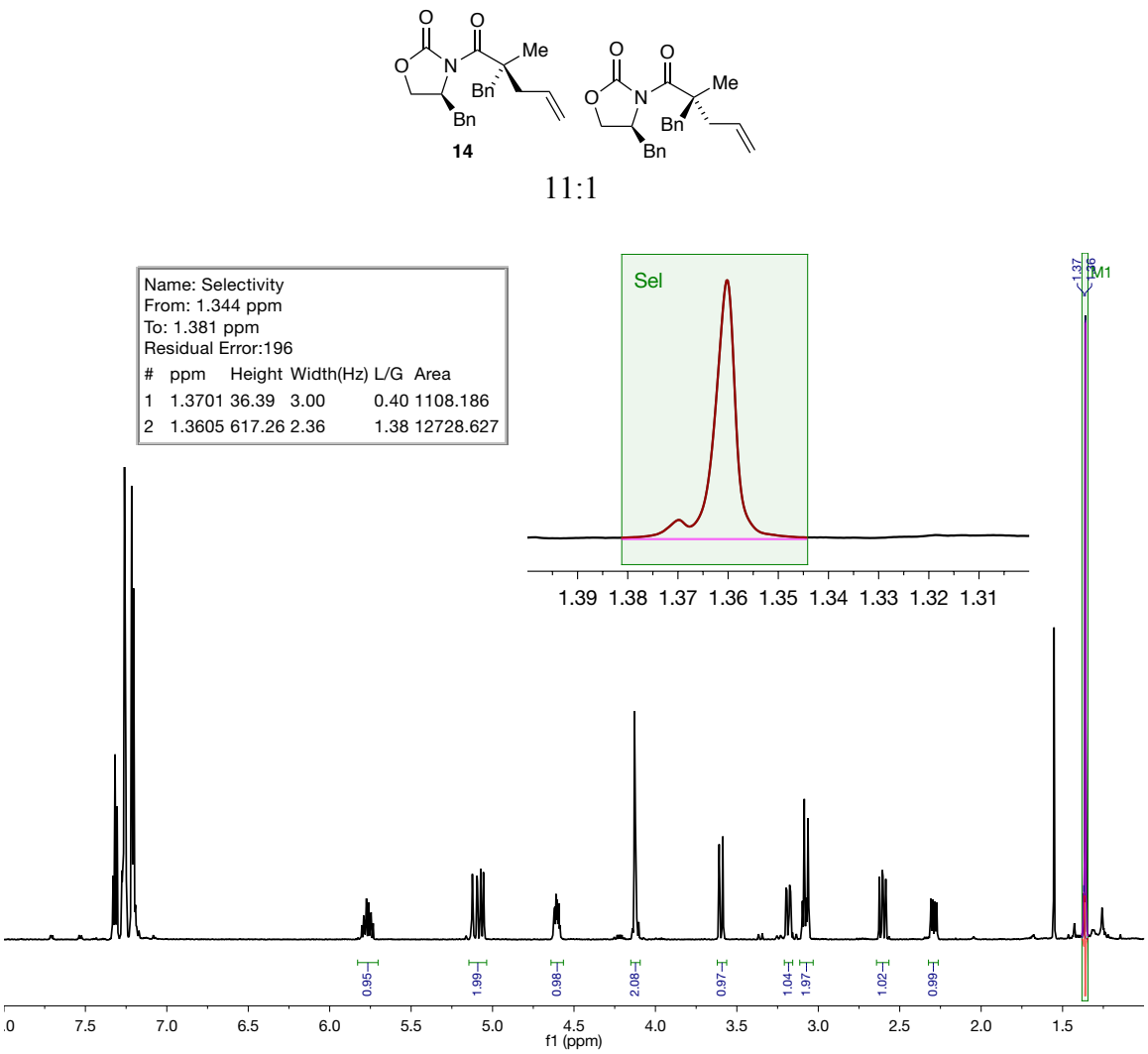


Figure A.2.109. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **13** and **29** in TMEDA. An isolated yield of 44% was obtained. The integration shows a 11:1 selectivity.

(4S)- 4-benzyl-3-((2S)-2-methyl-3-phenylpropanoyl)-2-oxazolidinone (**15**). To a solution of (*S*)-**9a** (0.30 mmol, 92.7 mg) in THF (1.5 mL) under Ar was added NaHMDS (0.40 mmol, 73.3 mg). Reaction was stirred under at –78 °C for 30 minutes. Methyl iodide (1.0 mmol, 62 μL) was injected and the mixture was stirred for 1 hour. The reaction was quenched by saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (20% EtOAc/hexanes) to afford the desired product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.24 – 7.18 (m, 5H), 4.52 (dddd, *J* = 9.8, 7.8, 3.3, 2.3 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.08 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.96 (ddd, *J* = 8.7, 7.7, 0.8 Hz, 1H), 3.25 (dd, *J* = 13.3, 3.4 Hz, 1H), 3.03 (dd, *J* = 13.3, 7.8 Hz, 1H), 2.78 – 2.68 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 3H).

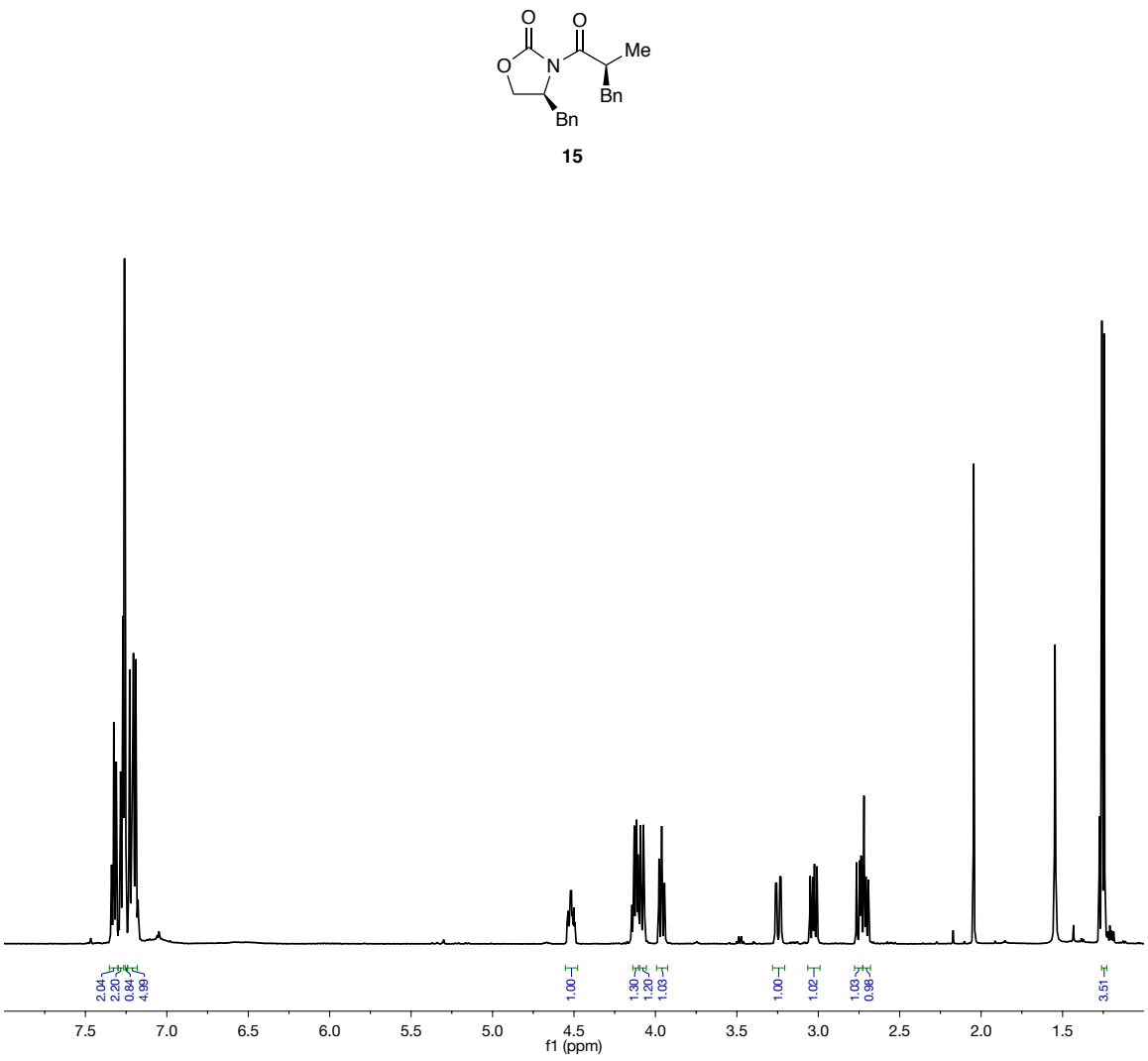


Figure A.2.110. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **15**.

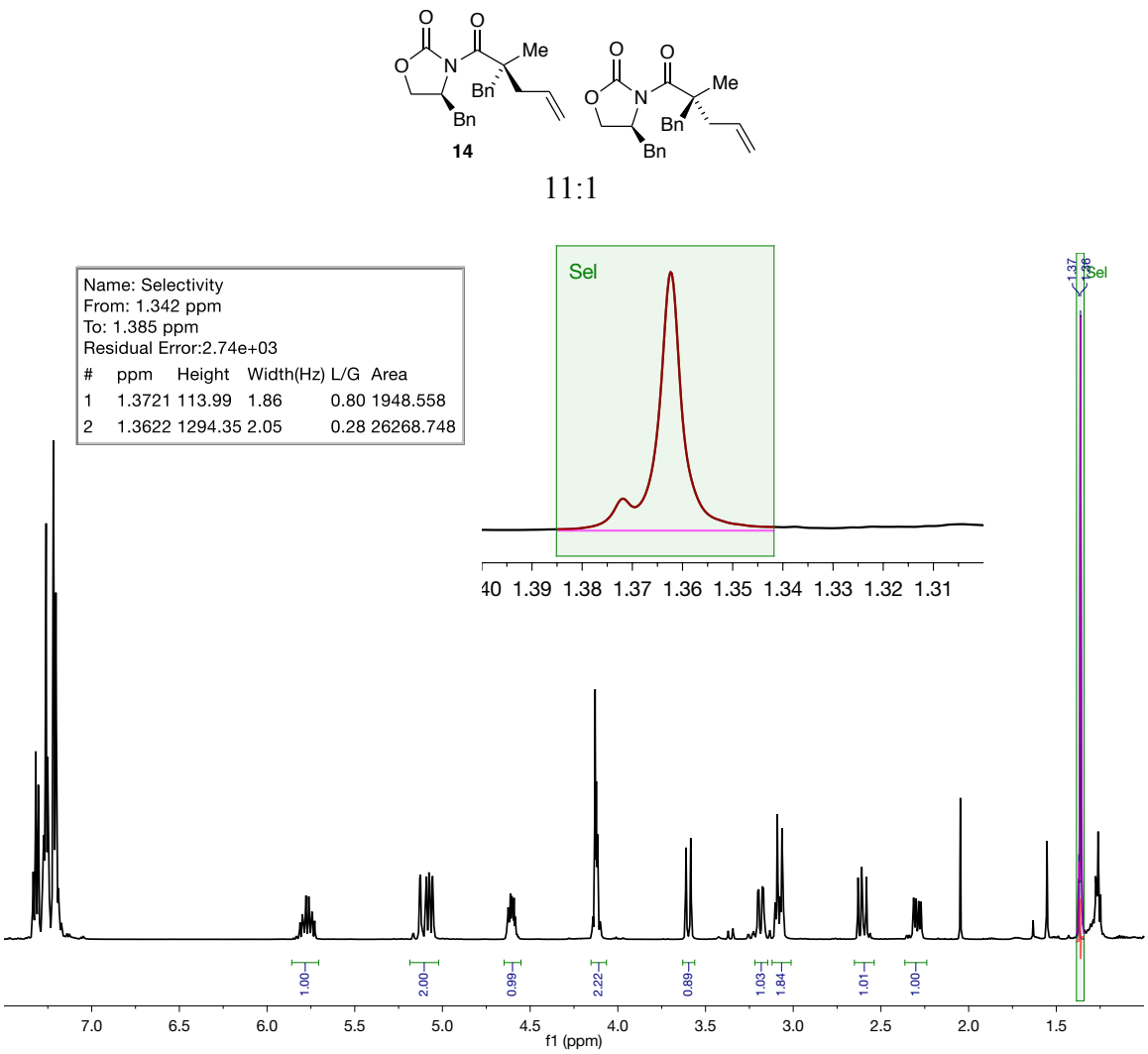
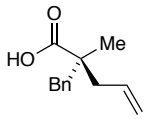


Figure A.2.111. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **14** prepared from **15**.
An isolated yield of 54%was obtained. The integration shows an 11:1 selectivity.

(*R*)-2-benzyl-2-methylpent-4-enoic acid (30). To a solution of **14** (0.050 mmol, 18 mg) in THF (0.45 mL) and water (0.15 mL) at 0 °C was added H_2O_2 (30%, 40 mL) dropwise and LiOH (2.4 mg) in water (0.10 mL). The reaction was warmed to 20 °C for 2 hr, cooled to 0 °C, and treated with Na_2SO_3 (56.8 mg) in water (0.3 mL) with stirring at 20 °C for 12 hr. The reaction was concentrated in vacuo, and its pH was adjusted to 13 using NaOH at 0 °C. The aqueous solution was extracted three times with CH_2Cl_2, and the pH was brought to 1 using concentrated HCl at 0 °C. The mixture was extracted three times with EtOAc, dried over $MgSO_4$, and concentrated in vacuo to afford 7 mg of product (69% combined yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 3H), 7.20 – 7.14 (m, 2H), 5.82 (ddt, *J* = 18.5, 9.2, 7.4 Hz, 1H), 5.17 – 5.09 (m, 2H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.78 (d, *J* = 13.4 Hz, 1H), 2.53 (ddt, *J* = 13.8, 6.9, 1.3 Hz, 1H), 2.21 (ddt, *J* = 13.7, 7.7, 1.2 Hz, 1H), 1.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.05, 137.33, 133.75, 130.35, 128.23, 126.77, 118.76, 47.48, 44.89, 43.33, 20.72. m/z calculated for $(M+H)^+$ 205.12231, found 205.12198. $[\alpha]^{22}$ = +12, c 0.35, CH_2Cl_2. An authentic sample was prepared using the procedure of Myers and coworkers. $[\alpha]^{22}$ = +24, c 0.5, CH_2Cl_2.

Kummer, D. A.; Chain, W. J.; Morales, M. R.; Quiroga, O.; Myers, A. G. *J. Am. Chem. Soc,* **2008**, *130*, 13231.



30

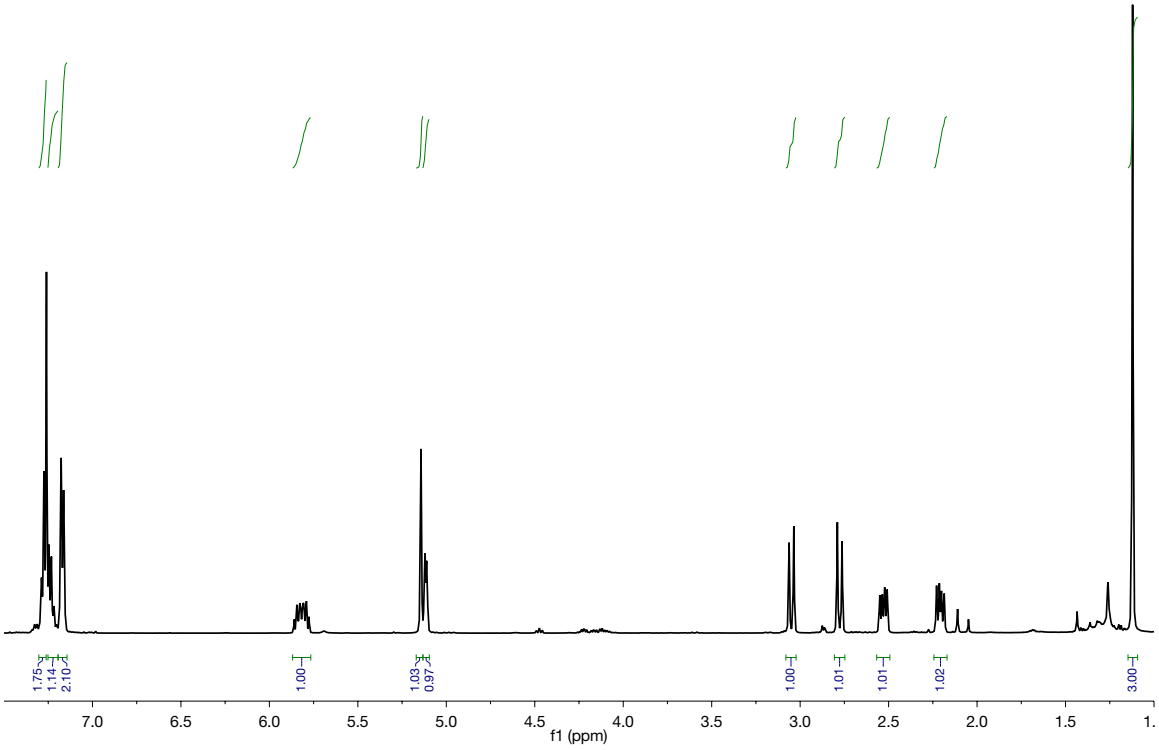


Figure A.2.112. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **30**.

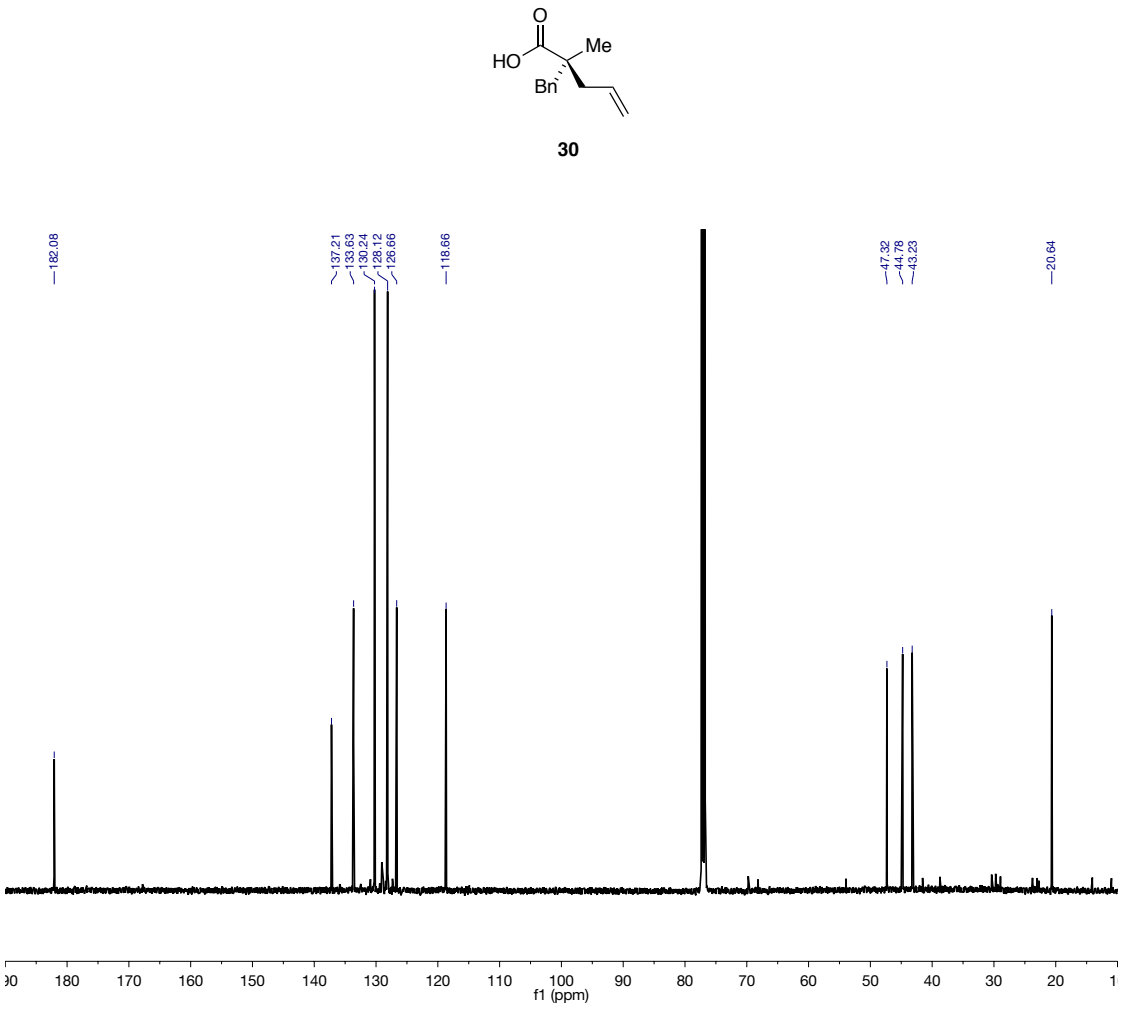


Figure A.2.113. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **30**.

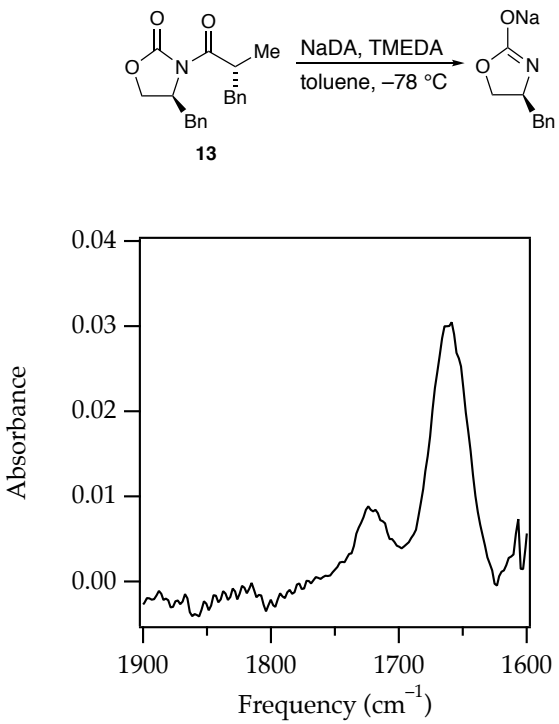


Figure A.2.114. IR spectrum of 0.010 M **13** and 0.013 M NaDA in 0.030 M TMEDA/toluene recorded at –78 °C. Using NaDA instead of NaHMDS results in exclusively deacylated product even at –78 °C. An isolated byproduct suggests competitive deprotonation on the auxiliary.

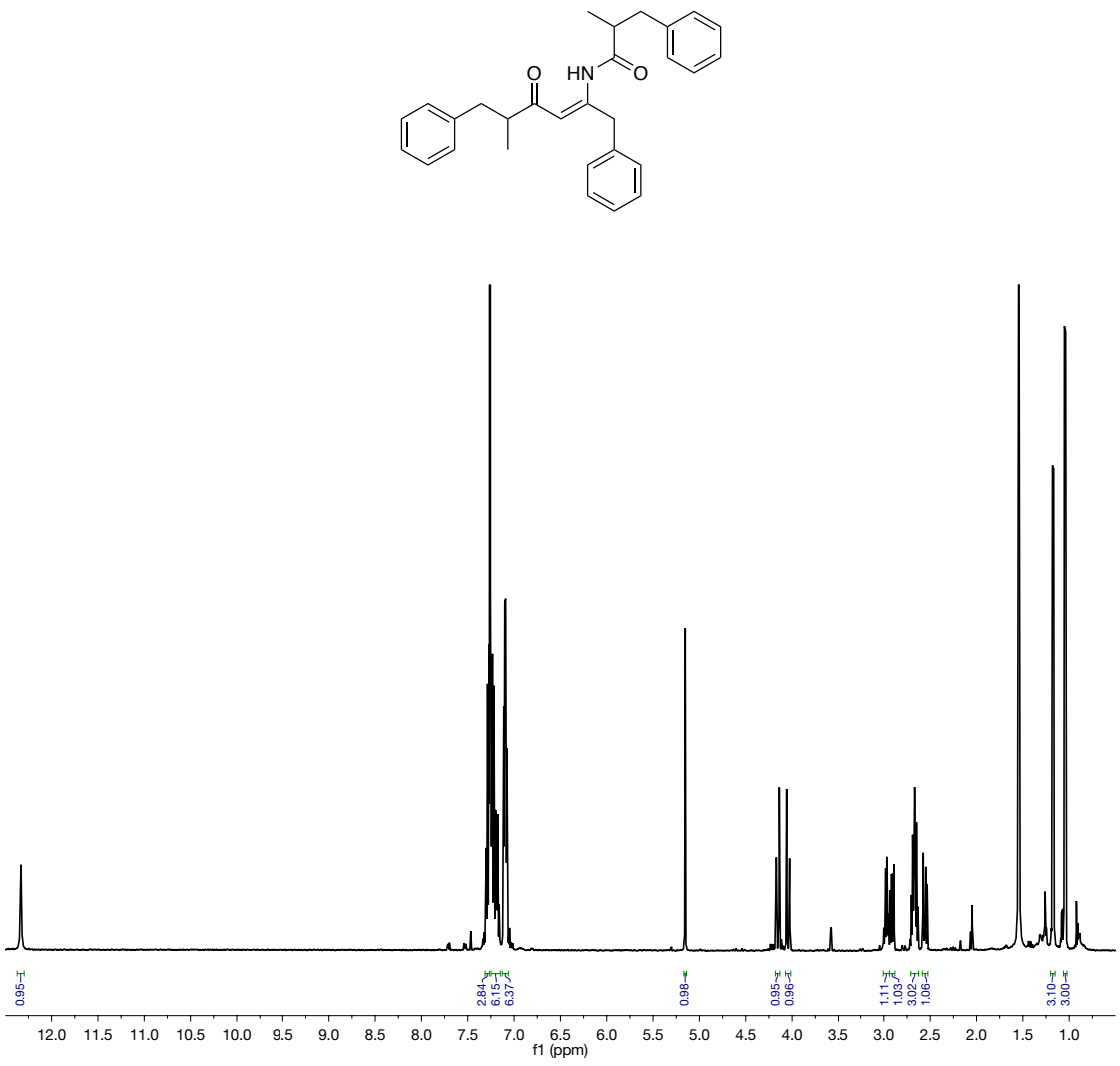


Figure A.2.115. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of backbone decomposition product.

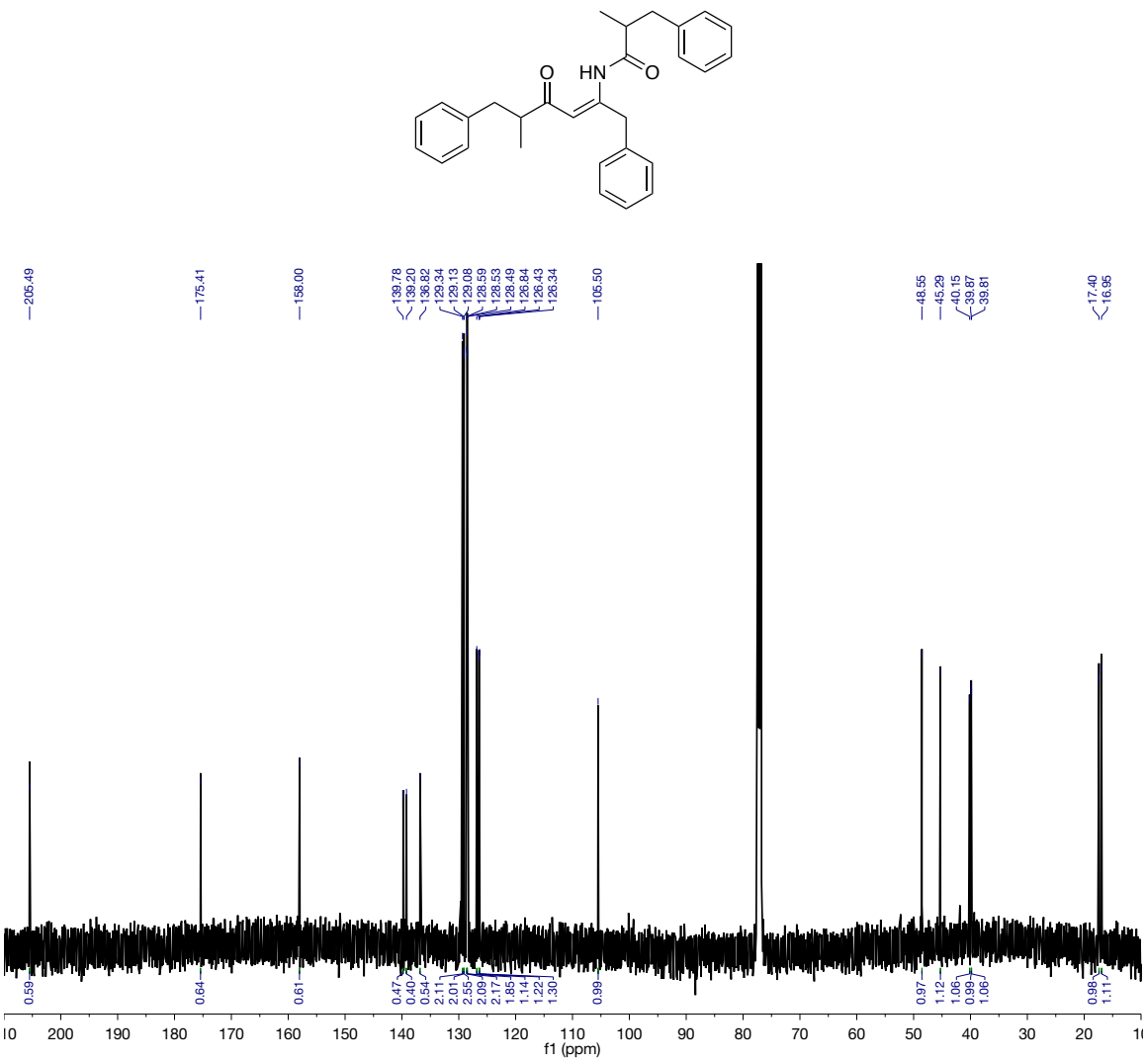


Figure A.2.116. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of backbone decomposition product.

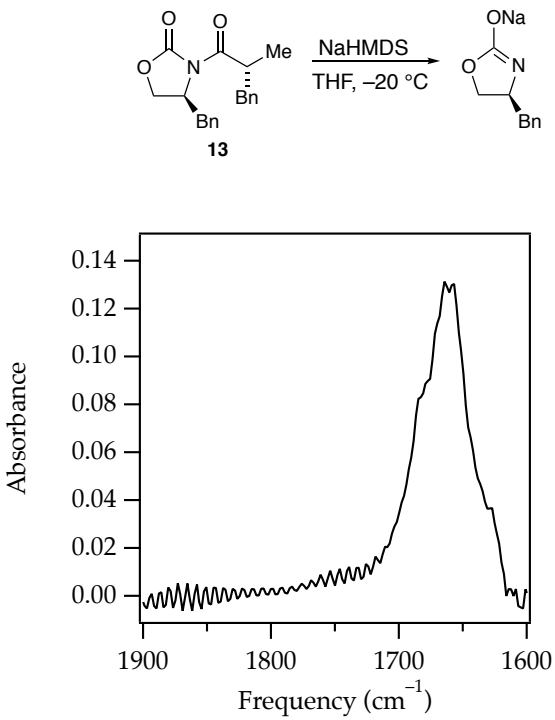


Figure A.2.117. IR spectrum of 0.010 M **13** and 0.015 M NaHMDS in THF recorded at –20 °C. Switching the solvent to THF produces decomposition product only.

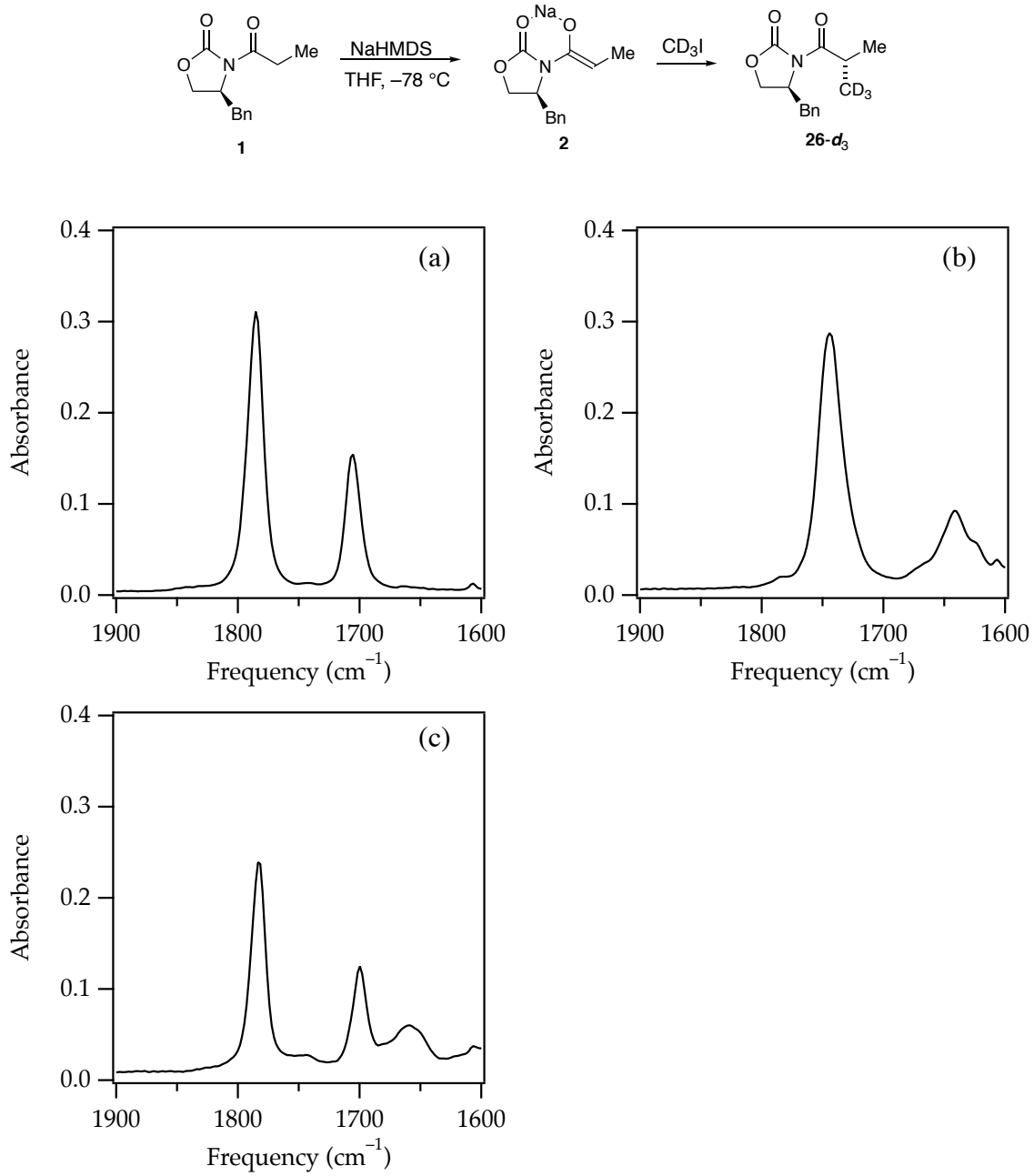


Figure A.2.118. IR spectra in THF recorded at –78 °C of (a) 0.10 M **1**; (b) 0.11 M **2**; (c) and 0.20 M **26-*d*$_3$**.

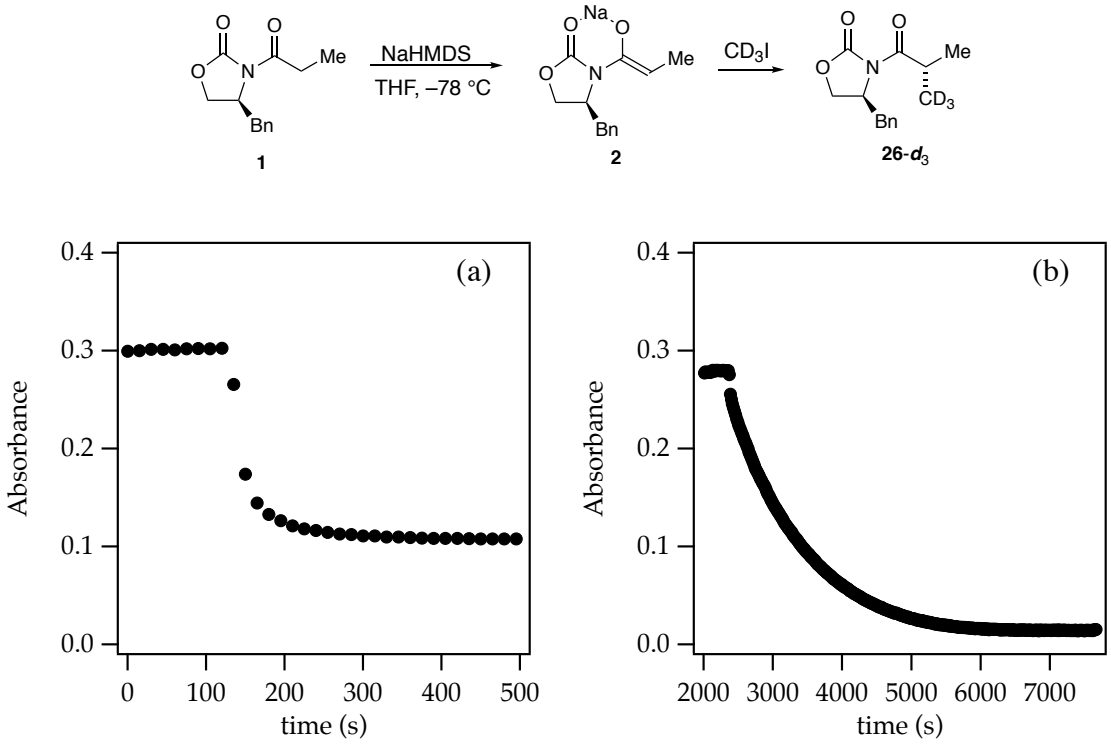


Figure A.2.119. IR spectrum in a solution of 0.10 M **1**, 0.11 M NaHMDS and 0.20 M CD_3I in THF recorded at –78 °C following (a) loss of **1**; (b) loss of **2**.

(4S)- 4-benzyl-3-((2R)-2-methylpropanoyl)-2-oxazolidinone-*d*$_3$ (26-*d*$_3$). To a solution of NaHMDS (0.55 mmol, 100.7 mg) in THF (5.0 mL), **1** (0.50 mmol, 116.5 mg) was added and reaction was stirred under Ar for 40 minutes at –78 °C. After injection of CD_3I (1.0 mmol, 62 μL), the mixture was stirred at –78 °C for 1.5 hours. The reaction was quenched by saturated NH_4Cl and extracted with three times EtOAc. The organic extracts were dried over $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (20% EtOAc/hexanes). The desired product was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.23 – 7.19 (m, 2H), 4.68 (ddt, *J* = 9.5, 7.5, 3.2 Hz, 1H), 4.21 (t, *J* = 9.1 Hz, 1H), 4.17 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.74 (q, *J* = 6.8 Hz, 1H), 3.27 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.77 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).

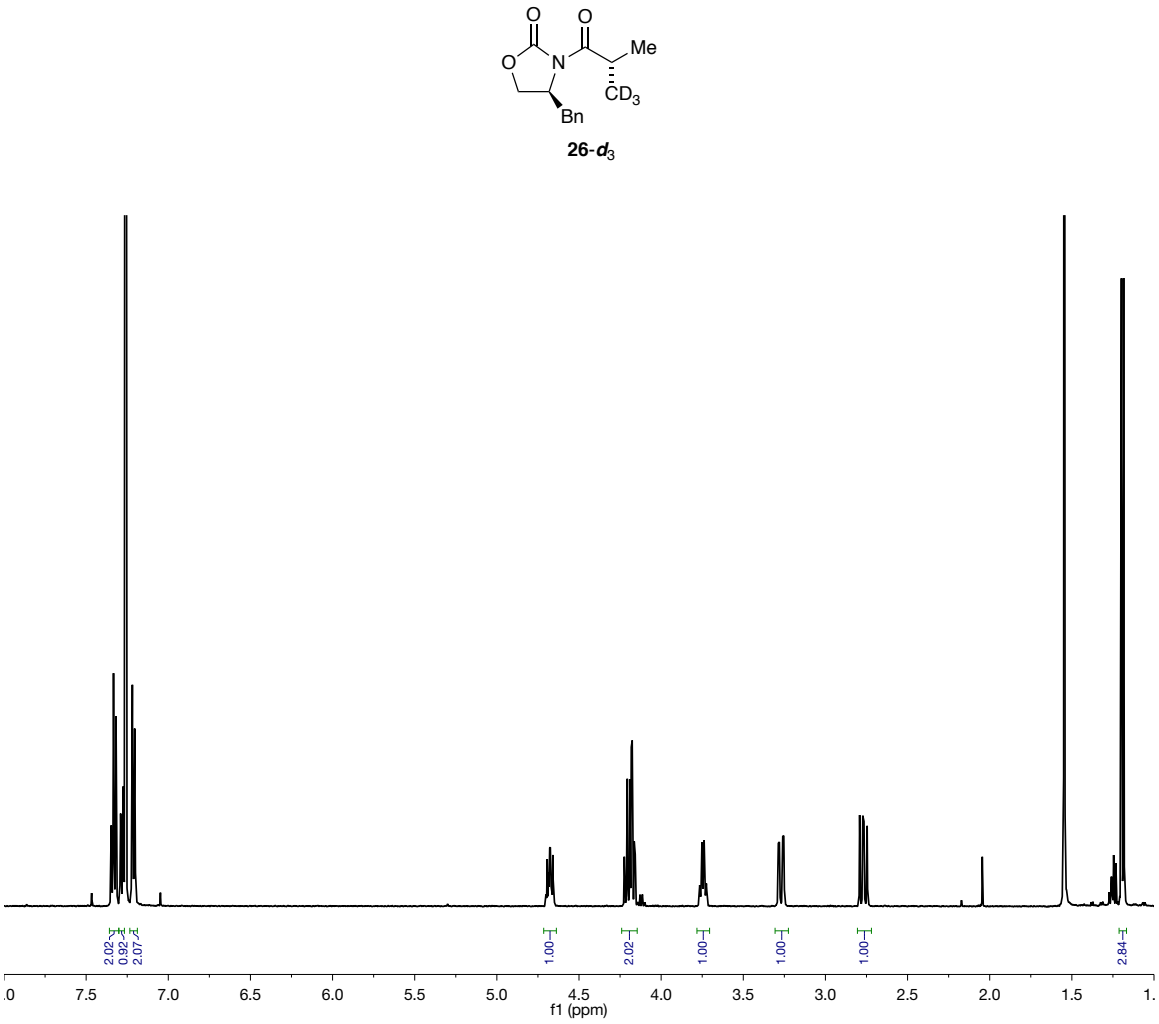


Figure A.2.120. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **26-*d*$_3$**.

(4S)- 4-benzyl-3-(2,2-dimethylpent-4-enoyl)-2-oxazolidinone (**31**). To a solution of NaHMDS (0.12 mmol, 22 mg) and TMEDA (0.30 mmol, 45 μL) in toluene (2 mL), **26-*d*$_3$** (0.060 mmol, 15 mg) was added and reaction was stirred under Ar for 0.5 hour at –20 °C. After injection of allyl bromide (1 mmol, 86 μL), the mixture was warmed to 0 °C over 2 hours. The reaction was quenched by saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (15% EtOAc/hexanes). The desired product was obtained in 57% yield (10 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 5.77 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.68 (ddt, *J* = 10.2, 7.3, 3.1 Hz, 1H), 4.17 (t, *J* = 9.0 Hz, 1H), 4.13 (dd, *J* = 9.0, 2.8 Hz, 1H), 3.26 (dd, *J* = 13.3, 3.3 Hz, 1H), 2.73 – 2.65 (m, 2H), 2.61 (dddd, *J* = 13.9, 7.3, 2.9, 1.5 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.59, 152.50, 135.82, 134.53, 129.57, 129.05, 127.40, 118.13, 66.36, 57.85, 45.27, 42.30, 38.19, 24.74.

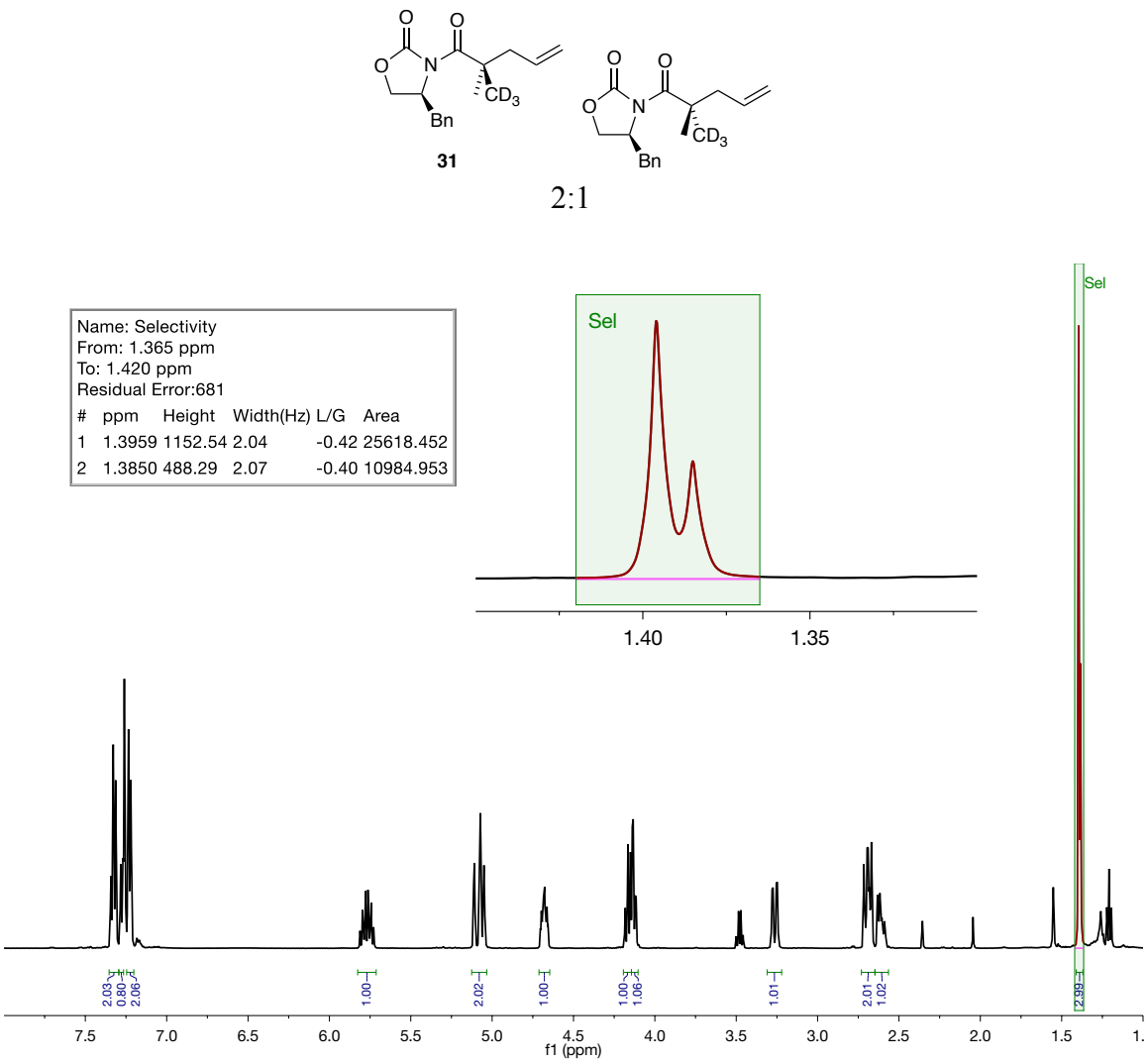


Figure A.2.121. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **31** prepared from **26-*d*$_3$**. The integration shows a 2:1 selectivity.

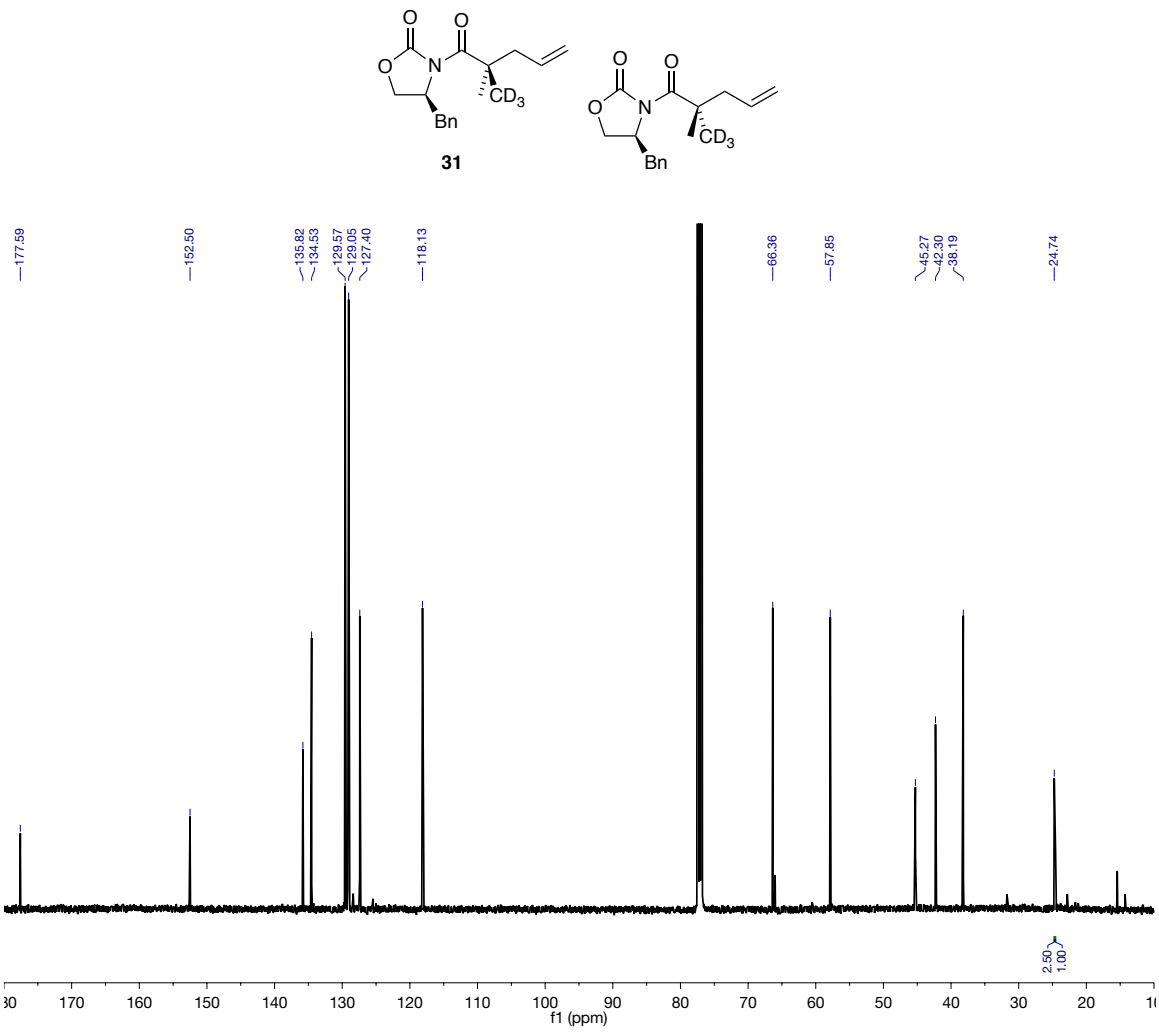


Figure A.2.122. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **31**.

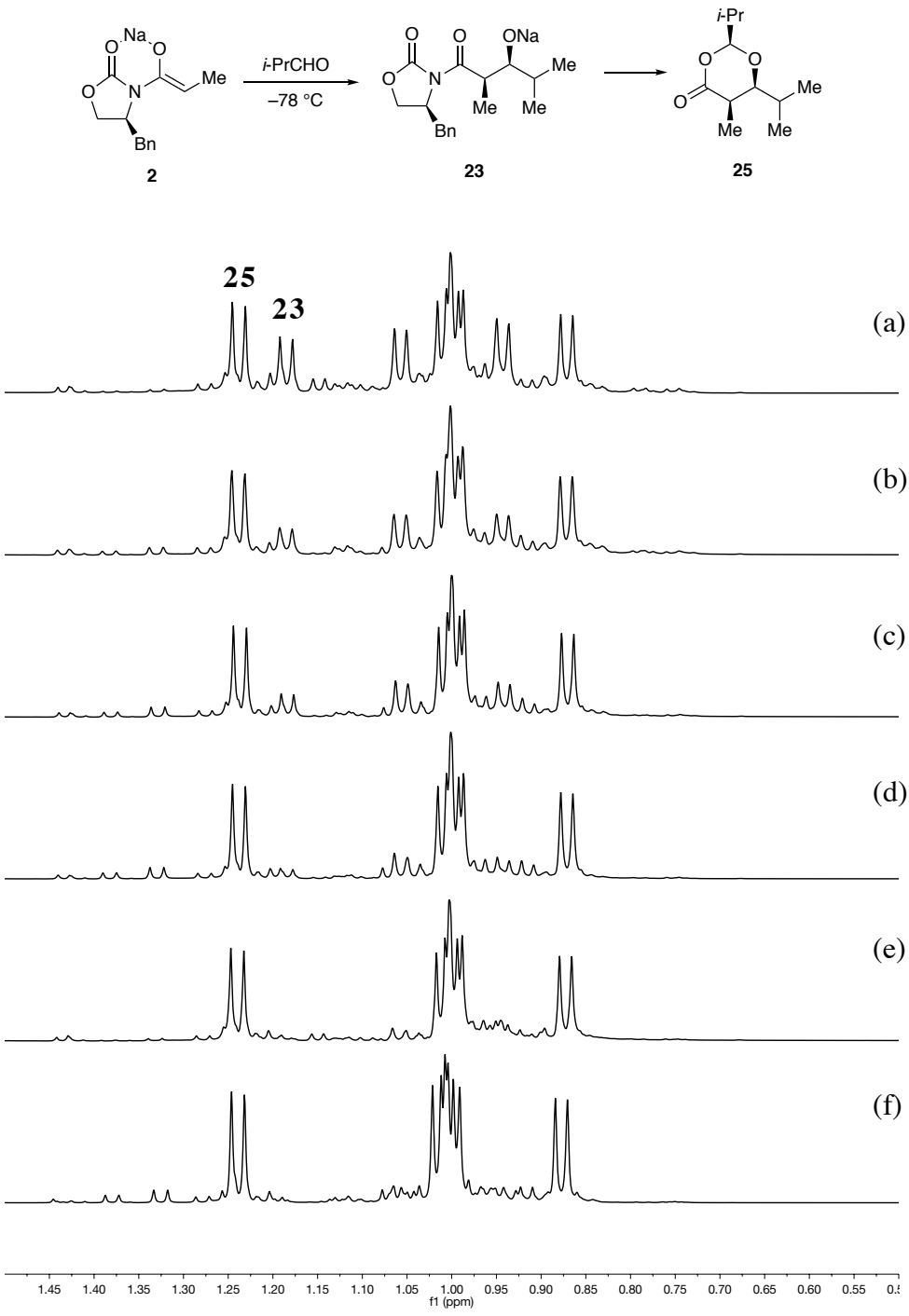


Figure A.2.123. ^{1}H NMR spectra recorded in $CDCl_3$ at rt of 0.10 M **2** and 0.30 M isobutyraldehyde in 0.30 M TMEDA/toluene, quenched with NH_4Cl after (a) 1 min; (b) 3 min; (c) 10 min; (d) 25 min; (e) 1 h; (f) 2 h at –78 °C. The regular aldol product is detected as the minor species and disappears as the reaction proceeds. Another major product is observed and isolated.

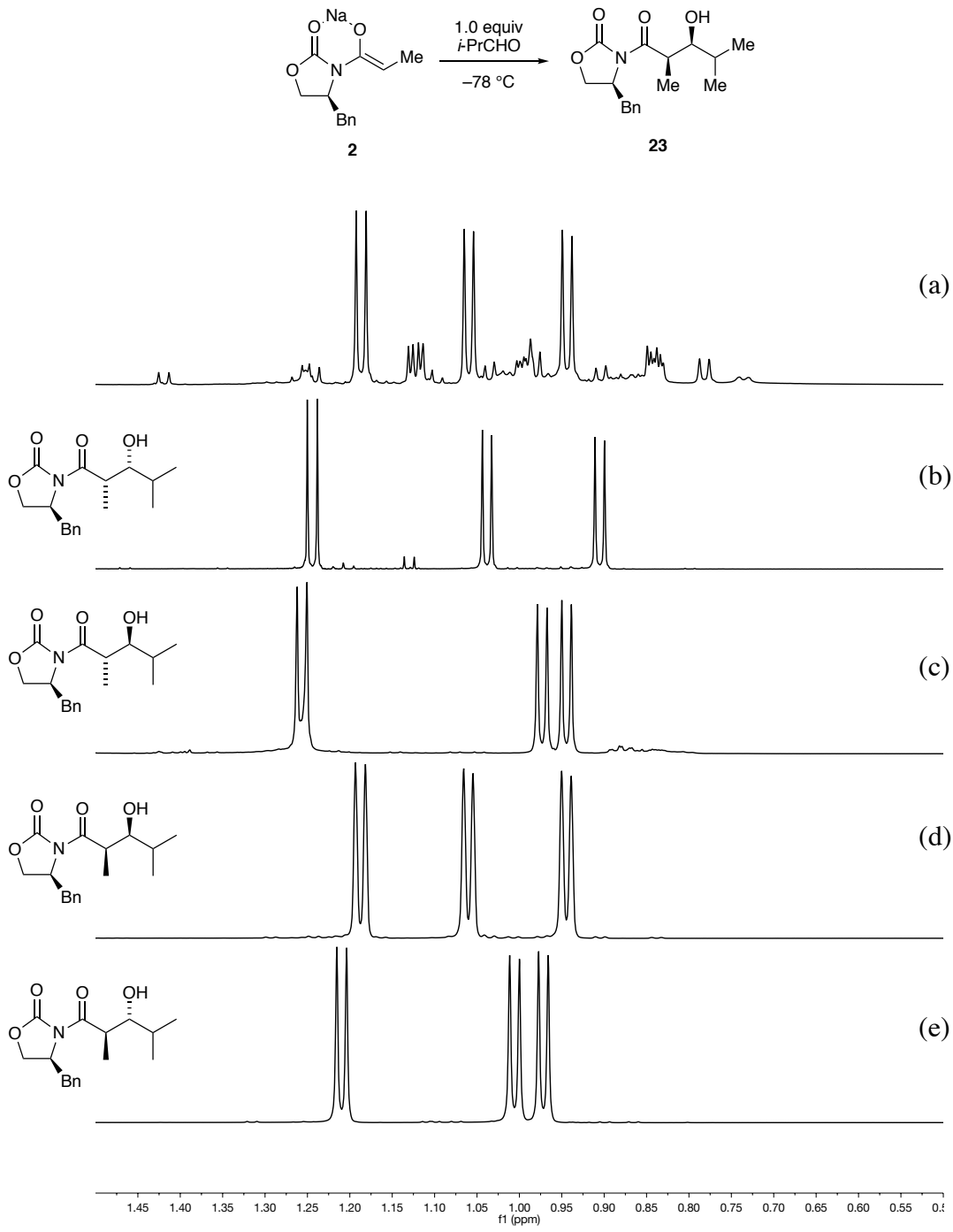


Figure A.2.124. ^{1}H NMR spectrum in $CDCl_3$ recorded at rt of (a) **23** prepared from adding 1 equivalent of isobutyraldehyde to **1**; (b) non-Evans syn; (c) Evans anti; (d) Evans syn; (e) non-Evans anti. The yield is only 15%. The majority of the products are starting material **2** and deacylated product.

Synthesis of 25.

To a solution of NaHMDS (0.3 mmol, 54.9 mg) and TMEDA (0.90 mmol, 144 μL) in toluene (3.0 mL) was added **1** (0.30 mmol, 69.9 mg) in 0.10 mL of toluene. After stirring under Ar for 30 min at –78 °C isobutyraldehyde (0.90 mmol, 82 μL) was injected and the mixture was stirred for 1 hr at –78 °C. After quenching with 1.0 mL saturated NH_4Cl and extracting three times with EtOAc, the organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography with 10% ethyl acetate in hexanes afforded 36.4 mg of **25** (61% combined yield). ^1H NMR showed a 17:1:0.7:0.4 mixture of **25** and three minor stereoisomers. ^1H NMR (599 MHz, $CDCl_3$) δ 5.06 (d, J = 4.2 Hz, 1H), 3.39 (dd, J = 9.0, 3.7 Hz, 1H), 2.73 (qd, J = 7.2, 3.7 Hz, 1H), 1.98 (hd, J = 6.9, 4.2 Hz, 1H), 1.84 (dh, J = 9.0, 6.6 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H), 1.01 – 0.97 (m, 9H), 0.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.94, 106.45, 82.07, 38.20, 32.71, 28.45, 18.67, 17.60, 16.17, 15.83, 11.74. m/z calculated for $(M+H)^+$ 201.14852, found 201.14824.

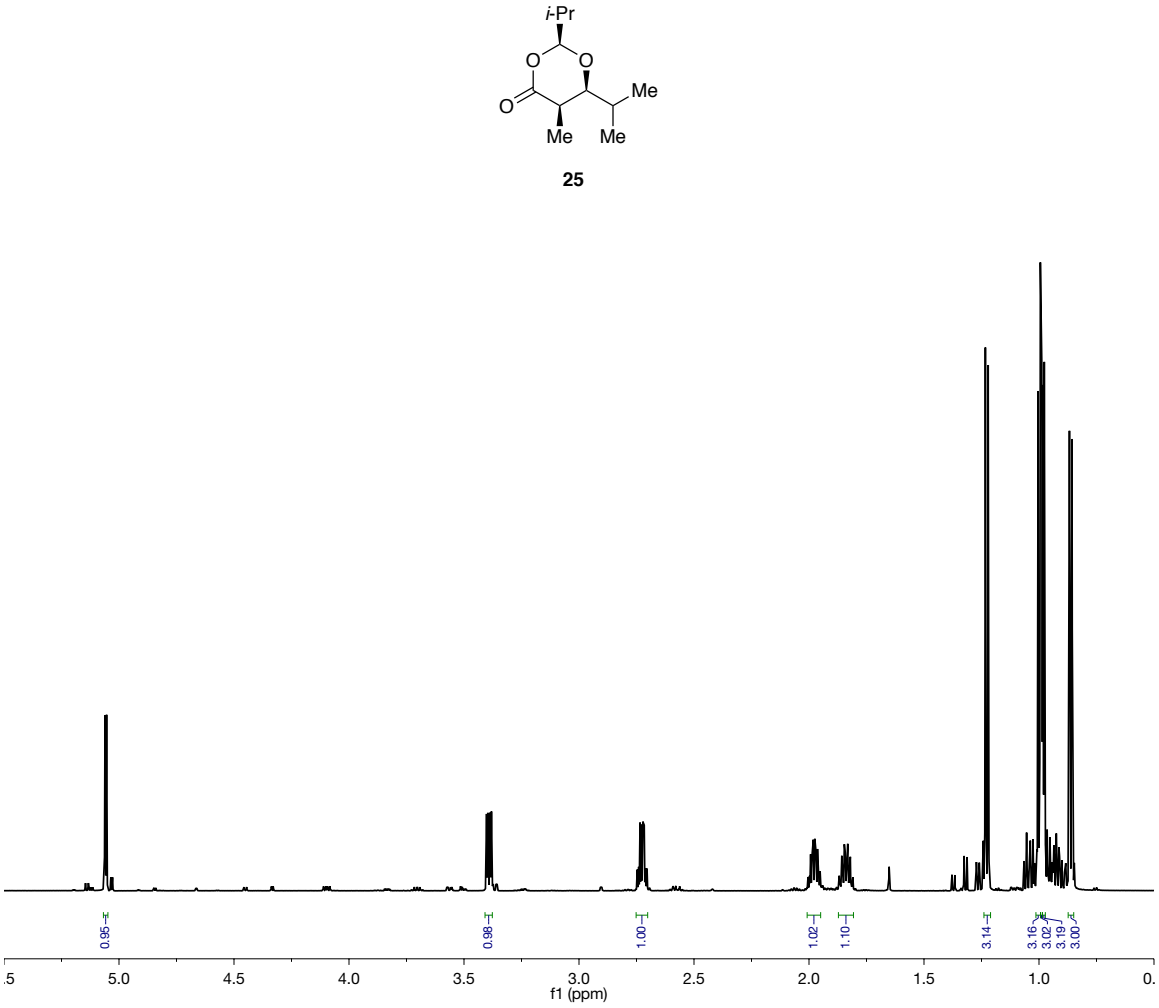


Figure A.2.125. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **25** prepared from (*S*)-**2** in TMEDA reacting with 3 equivalents of isobutyraldehyde. An isolated yield of 61% is obtained. Integration provides a diastereo selectivity of 17:1:0.7:0.4.

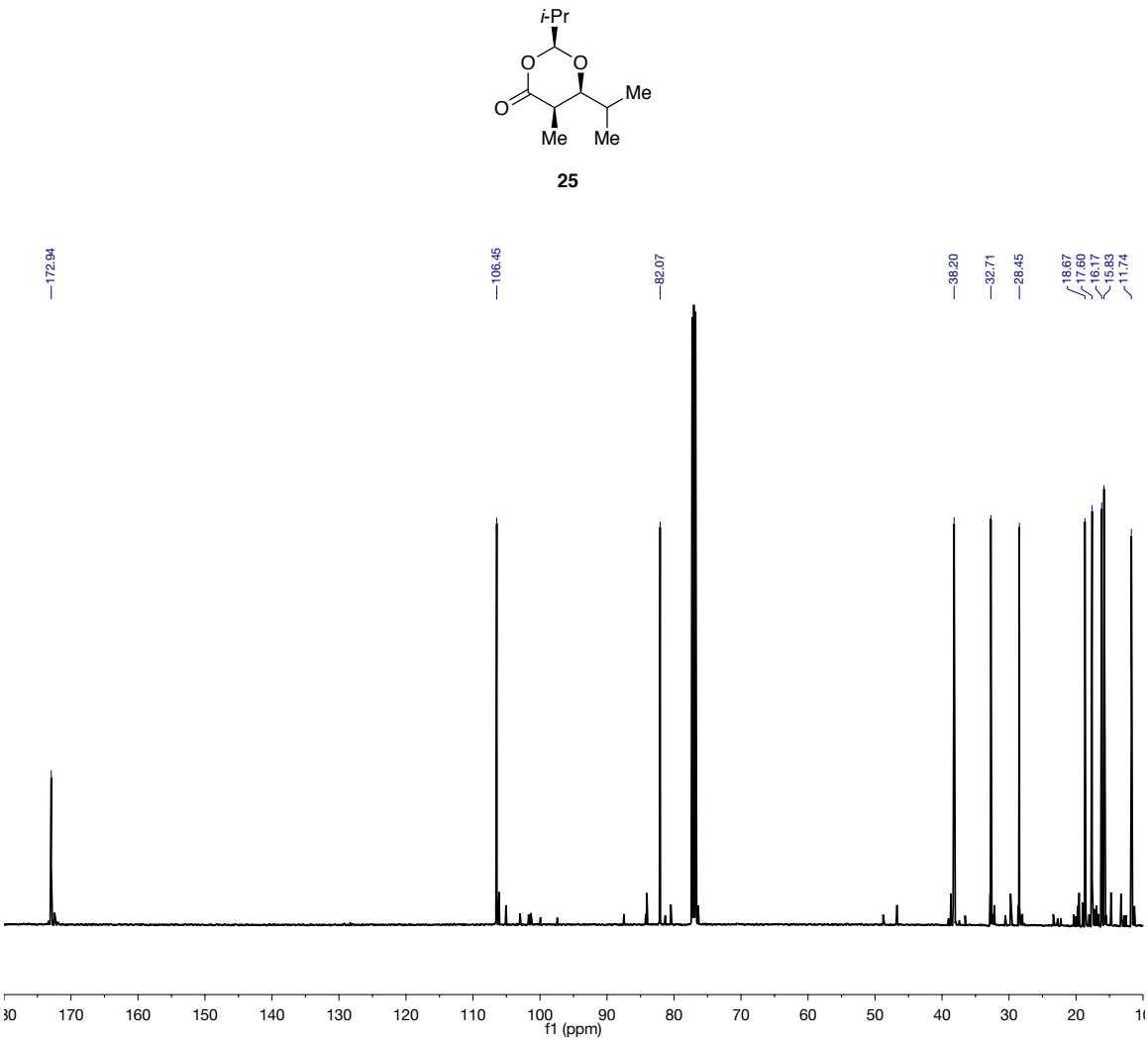
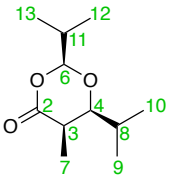


Figure A.2.126. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **25**.

Parameter	Value
1 Solvent	cdcl3
2 Temperature	23.0
3 Pulse Sequence	ROESYAD
4 Number of Scans	8
5 Receiver Gain	32
6 Relaxation Delay	1.5000
7 Pulse Width	8.2500
8 Acquisition Time	0.1500



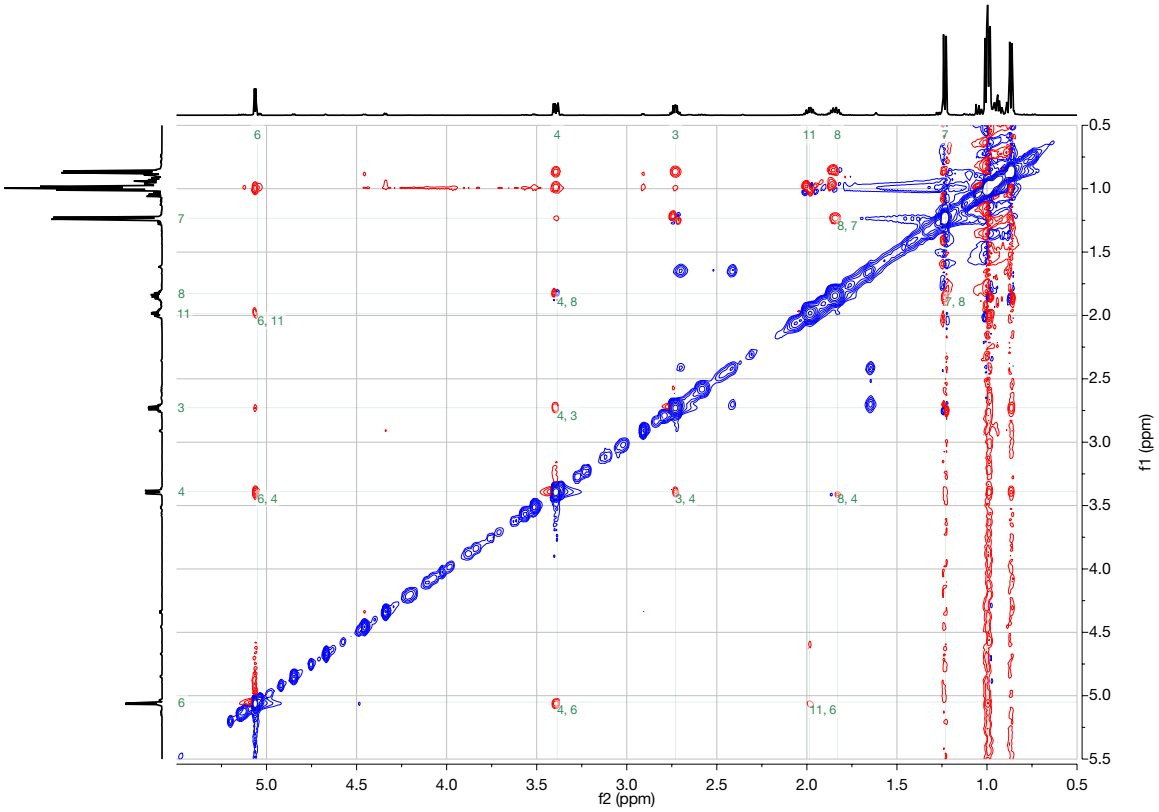


Figure A.2.127. ROESY spectrum of **25** in $CDCl_3$ recorded at rt.

Table A.2.3. ^{1}H and ^{13}C chemical shift assignments for **25**.

Atom #	δC, ppm	δH, ppm	ROESY
2	172.94		
3	38.20	2.73	4, 7, 9
4	82.07	3.39	3, 6, 8, 9, 10
6	106.45	5.05	4, 11, 12
7	18.67	1.23	3, 8
8	28.45	1.83	4, 7, 9, 10
9	11.74	0.84	3, 4, 8
10	15.83	0.96	4, 8
11	32.71	1.98	6, 12
12	16.17	0.98	6, 11
13	17.60	0.99	

The strong correlation between H#4 and H#6 through space is only viable by a 1, 3 diaxial interaction and thus sets the stereo center of C#6.

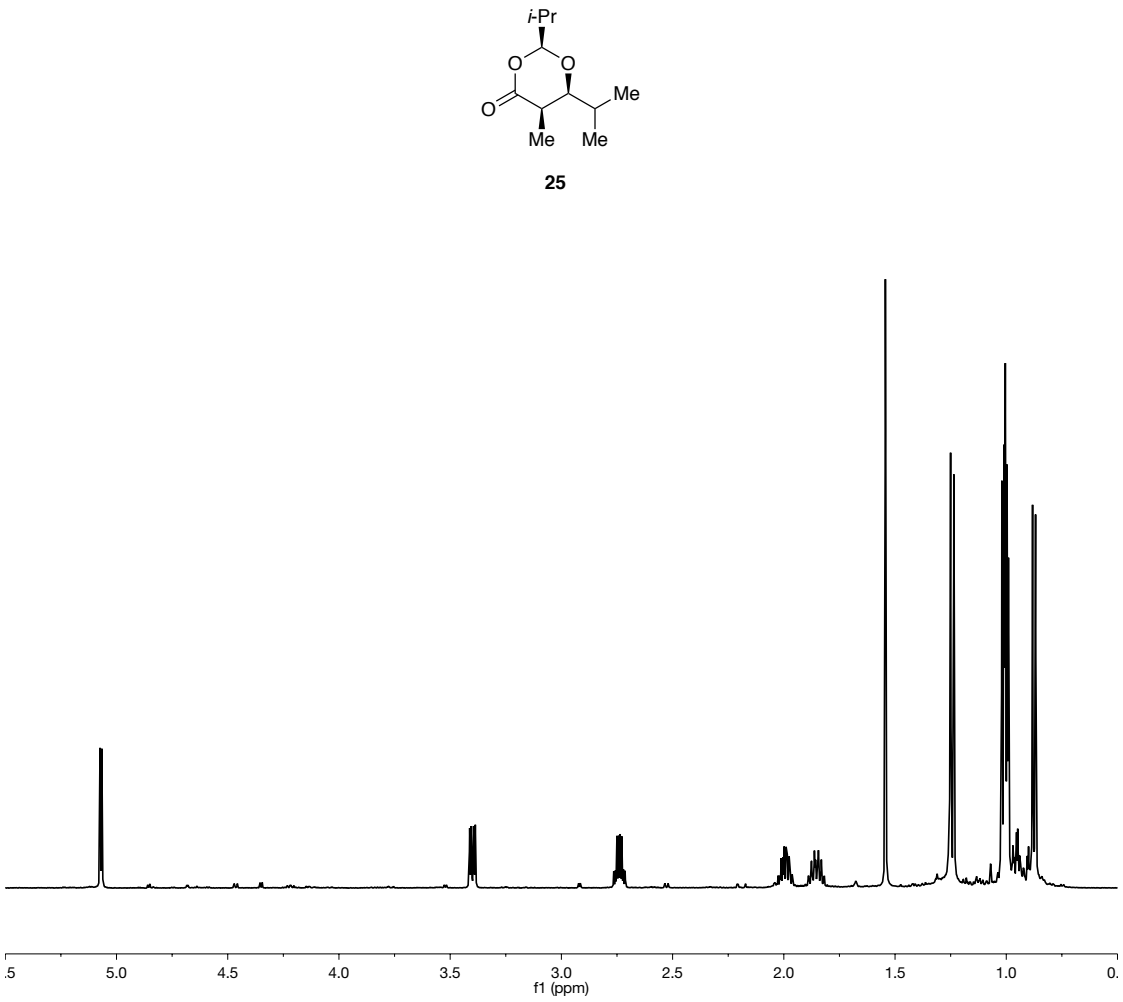


Figure A.2.128. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 0.10 M **25** prepared from **23** reacting with 1 equivalent of isobutyraldehyde. An isolated yield of 59% is obtained. The minor isomers are not observed in ^{1}H NMR.

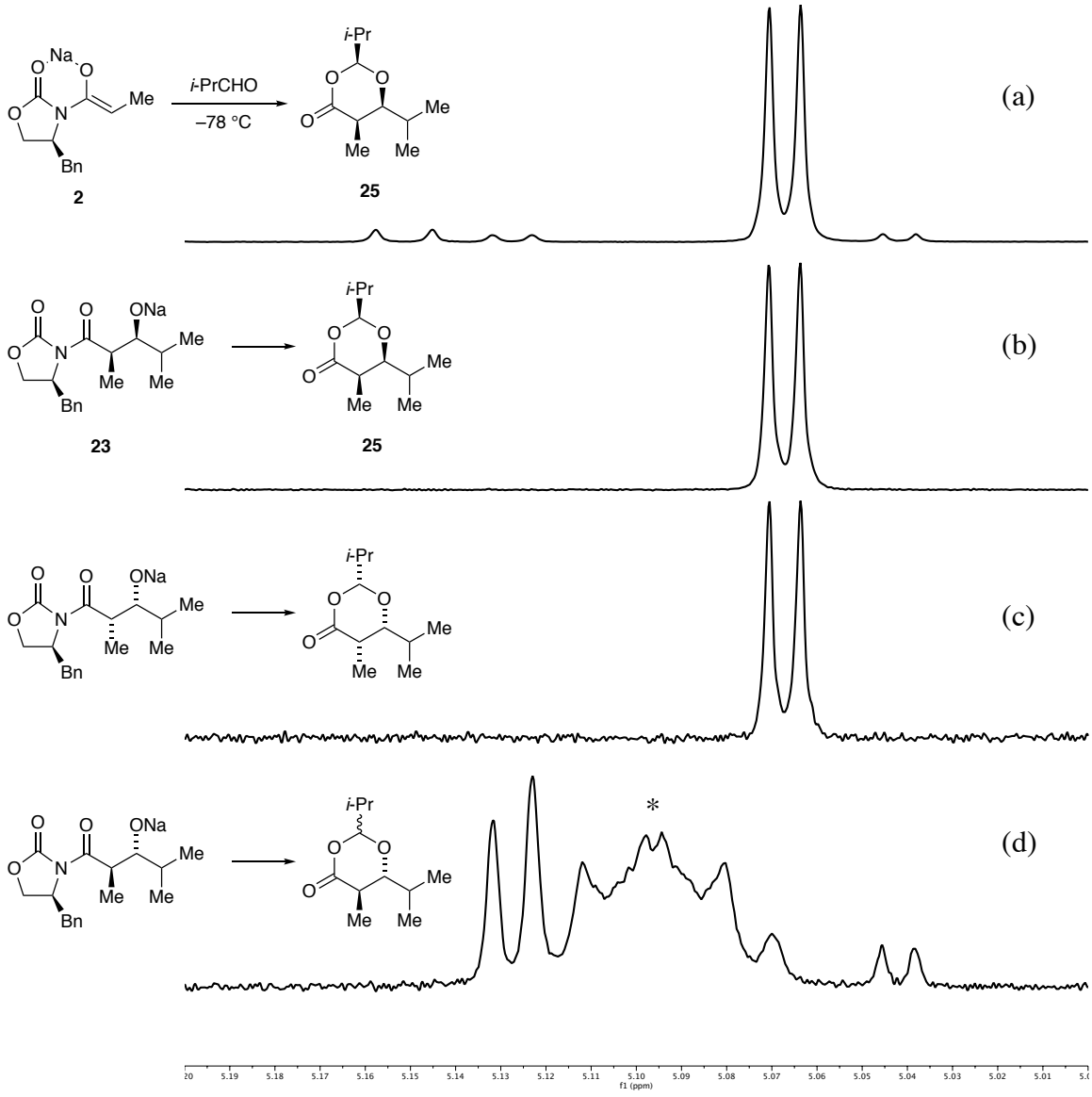


Figure A.2.129. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **25** prepared from isobutyraldehyde in TMEDA reacting with (a) (*S*)-**2**; (b) **23**; (c) Evans syn aldolate; (d) Evans anti aldolate.

* Side product

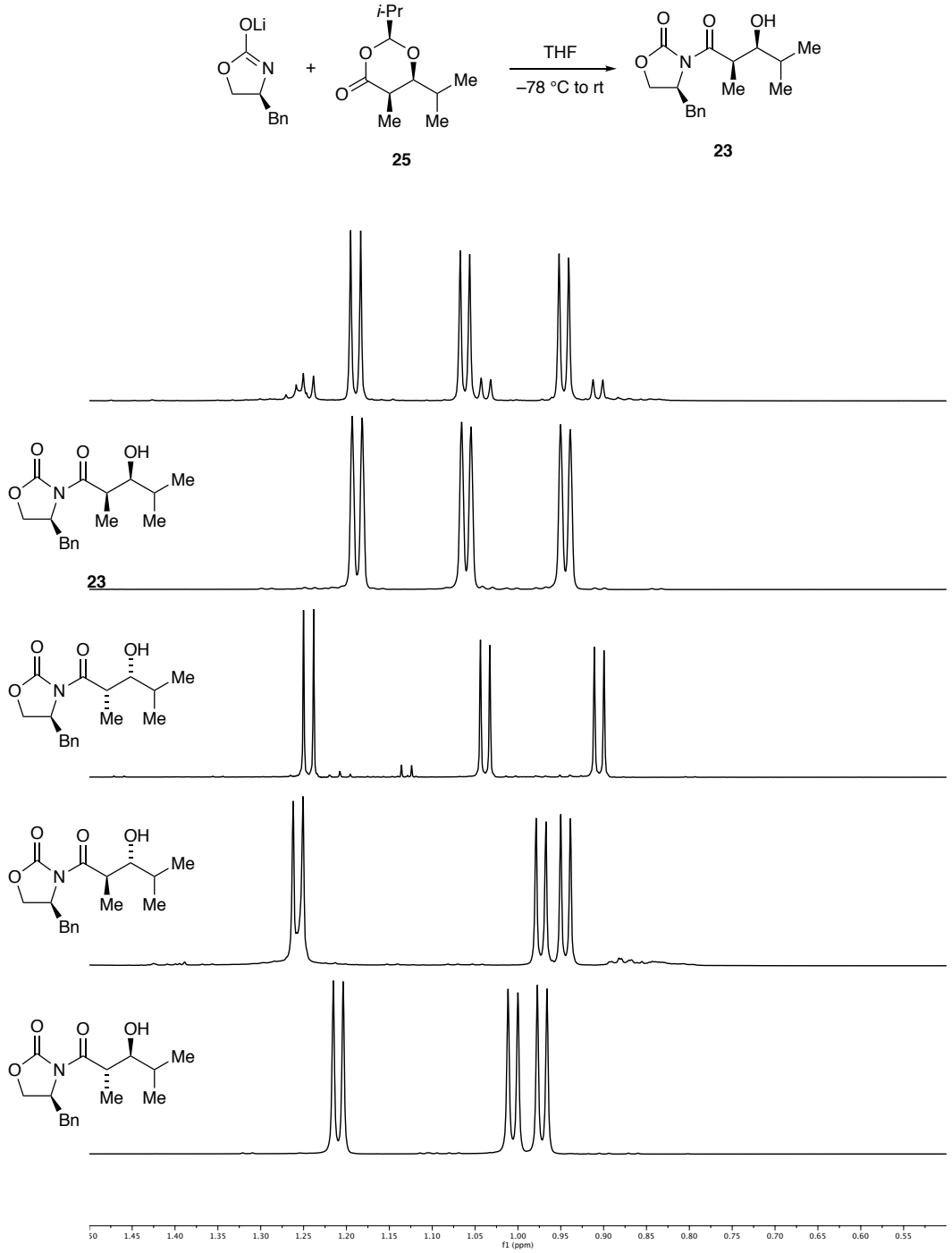


Figure A.2.130. ^{1}H NMR spectrum in $CDCl_3$ recorded at rt of (a) **23** prepared from adding lithiated auxilliary to **25**; (b) non-Evans syn; (c) Evans syn; (d) non-Evans anti; (e) Evans anti.

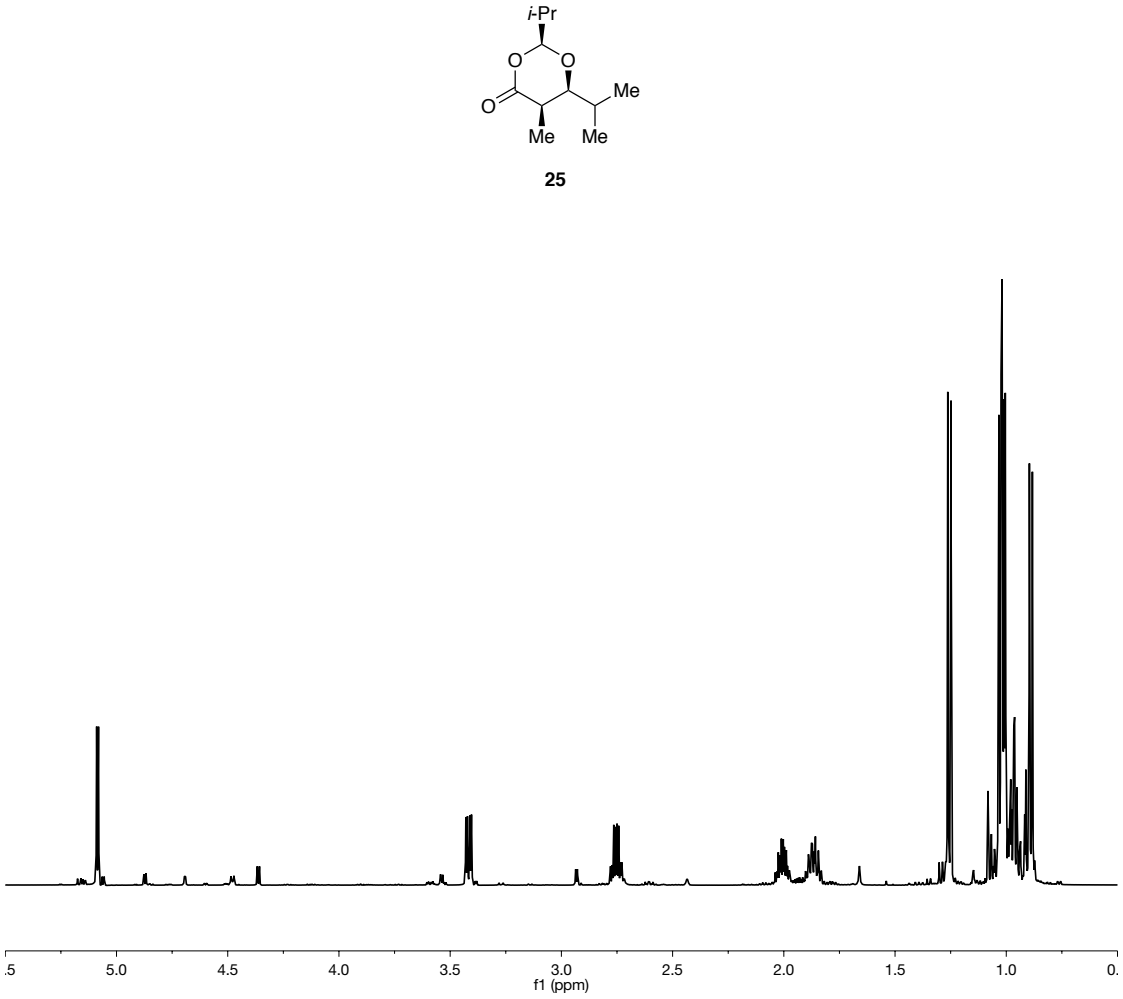


Figure A.2.131. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 0.10 M **25** prepared from **6** reacting with 3 equiv of isobutyraldehyde. An isolated yield of 58% is obtained. Integration provides a selectivity of 16:1:0.7:0.6.

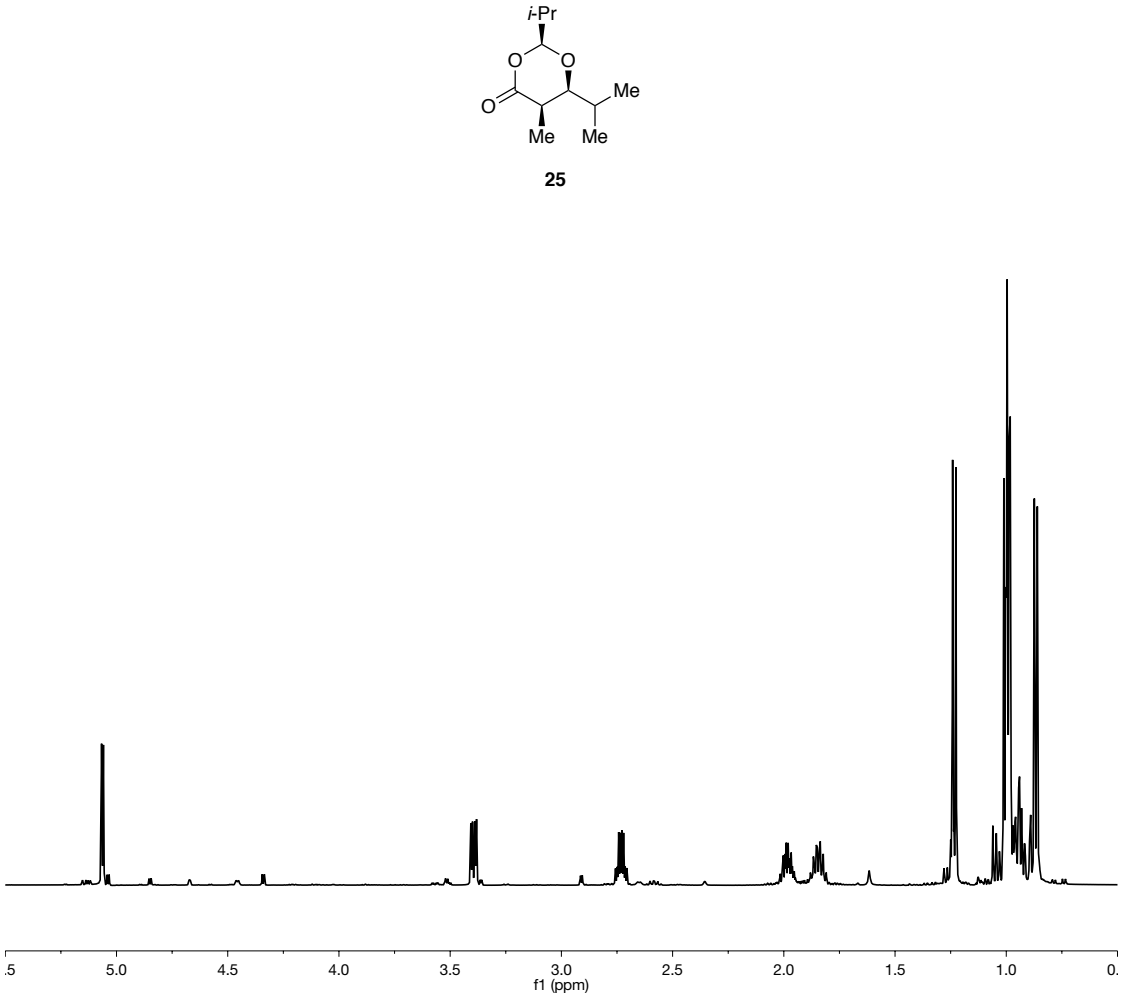


Figure A.2.132. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 0.10 M **25** prepared from **7** in TMEDA reacting with 3 equivalent of isobutyraldehyde. An isolated yield of 57% is obtained. Integration provides a selectivity of 13:1:0.5:0.5.

(4*S*)-4-benzyl-3-(2-methyl-3-(phenylamino)-3-(4-(trifluoromethyl)phenyl)propanoyl) oxazolidinone (**32**). To a solution of NaHMDS (0.11 mmol, 20.2 mg) and TMEDA (0.22 mmol, 33 μL) in toluene (5.0 mL), **1** (0.10 mmol, 23.3 mg) was added. After stirring for 1.5 hr under Ar at –78 °C, complex **38** formed from imine **37** (0.10 mmol, 24.9 mg) and BF_3 (0.10 mmol, 19 μL) was injected as a slush. The reaction was stirred for 1 hour at –78 °C, quenched with saturated NH_4Cl, and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$, concentrated in vacuo, and purified by flash chromatography (10% EtOAc/hexanes/3% Et_3N). Adduct **32** (38 mgs) was obtained 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 –6.61 (m, 14H), 5.03 (t, *J* = 5.1 Hz, 1H), 4.72 (tt, *J* = 8.4, 3.2 Hz, 1H), 4.32 (qd, *J* = 6.9, 4.6 Hz, 1H), 4.24 (t, *J* = 8.7 Hz, 1H), 4.15 (dd, *J* = 9.1, 3.0 Hz, 1H), 2.91 (dd, *J* = 13.7, 3.3 Hz, 1H), 2.49 (dd, *J* = 13.7, 8.9 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.26, 153.38, 146.65, 134.62, 129.31, 129.28, 128.96, 127.46, 127.35, 125.56, 118.19, 113.64, 66.22, 58.08, 54.99, 43.95, 37.34, 10.51. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.36 (major), -62.47 (minor).

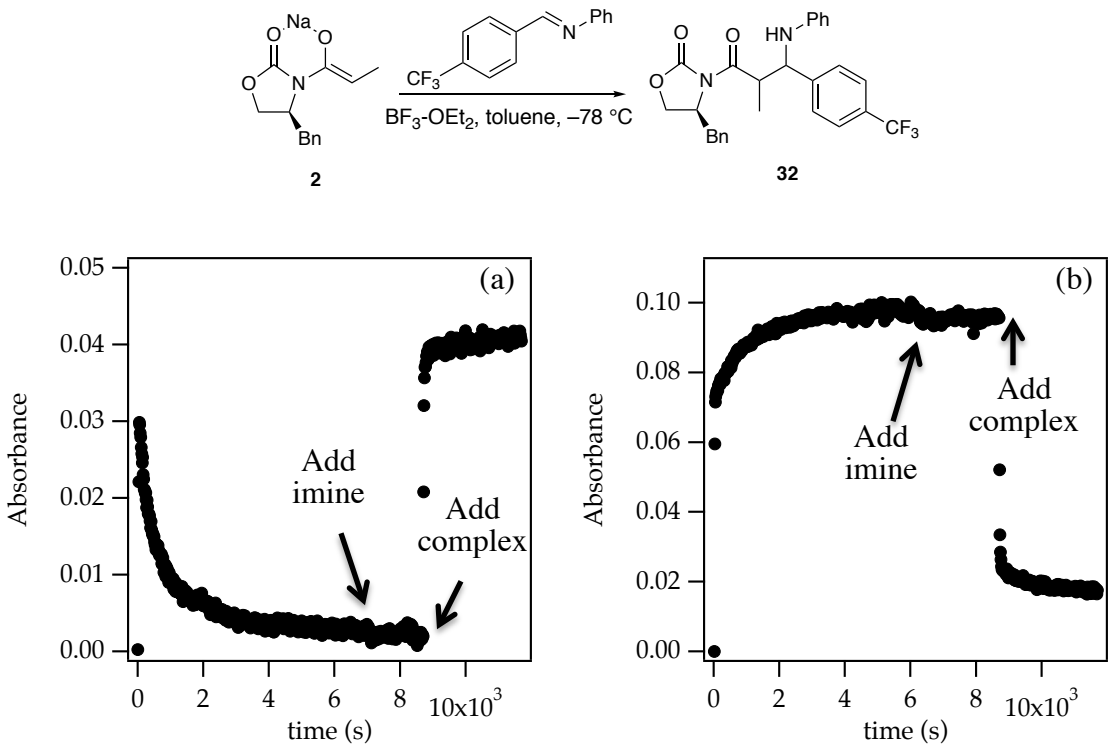


Figure A.2.133. IR spectra from a solution of 0.020 M **2** in toluene at –78 °C with first 0.020 M imine and then 0.020 M imine-BF_3 complex added, following (a) auxiliary C=O peak; (b) enolate peak. Adding only imine to enolate **2** shows no reactivity. Aza-aldol reaction occurs after imine-BF_3 complex addition.

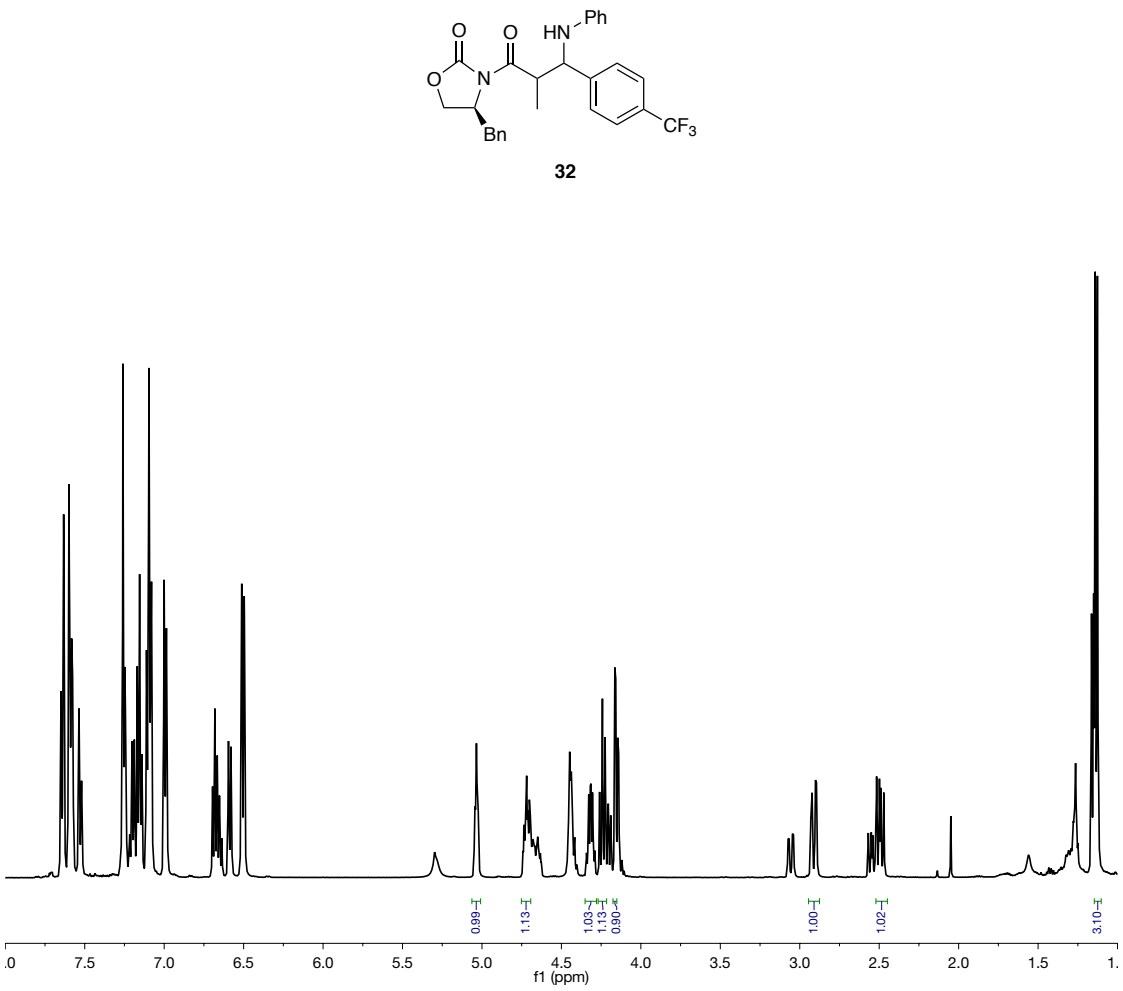


Figure A.2.134. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **32**.

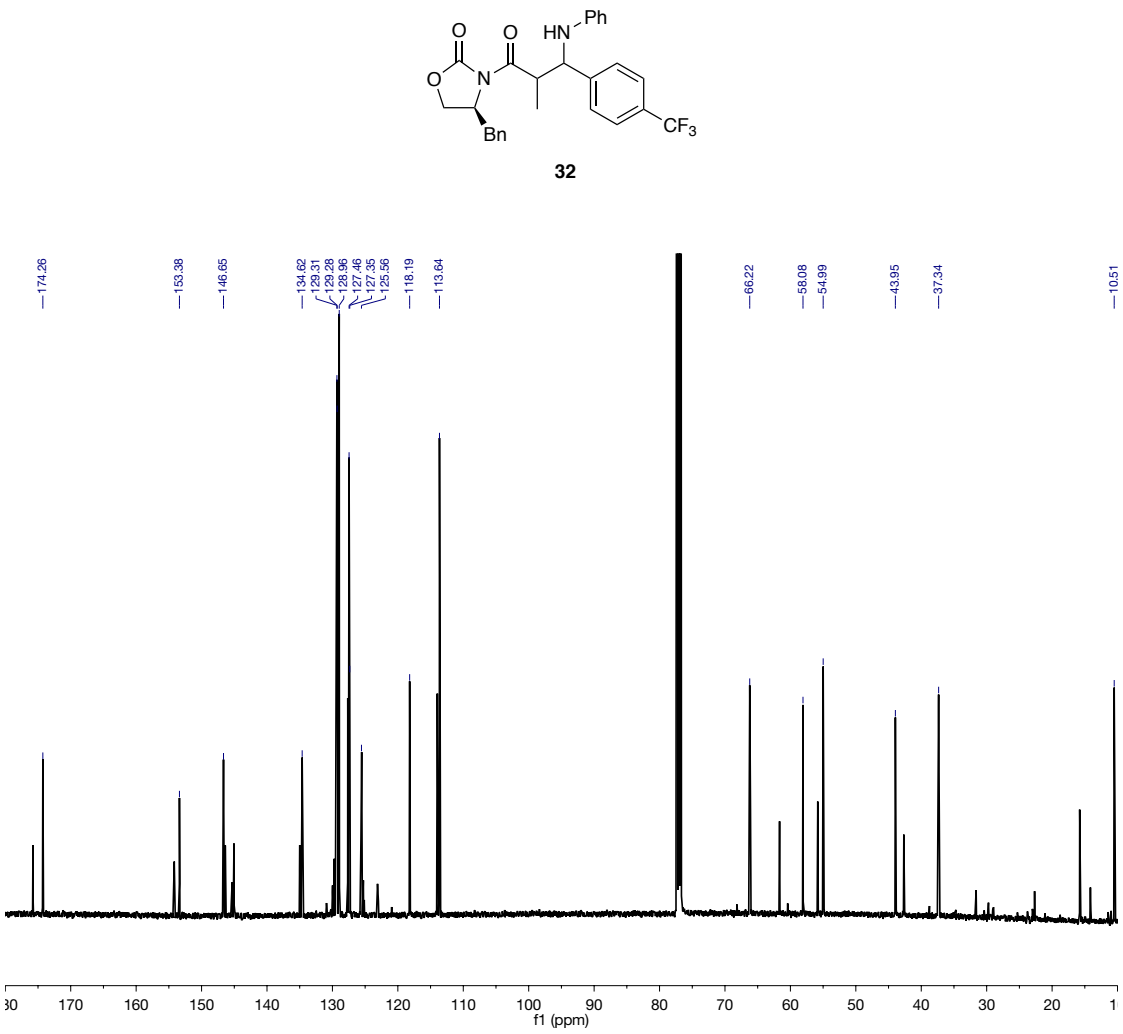


Figure A.2.135. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **32**.

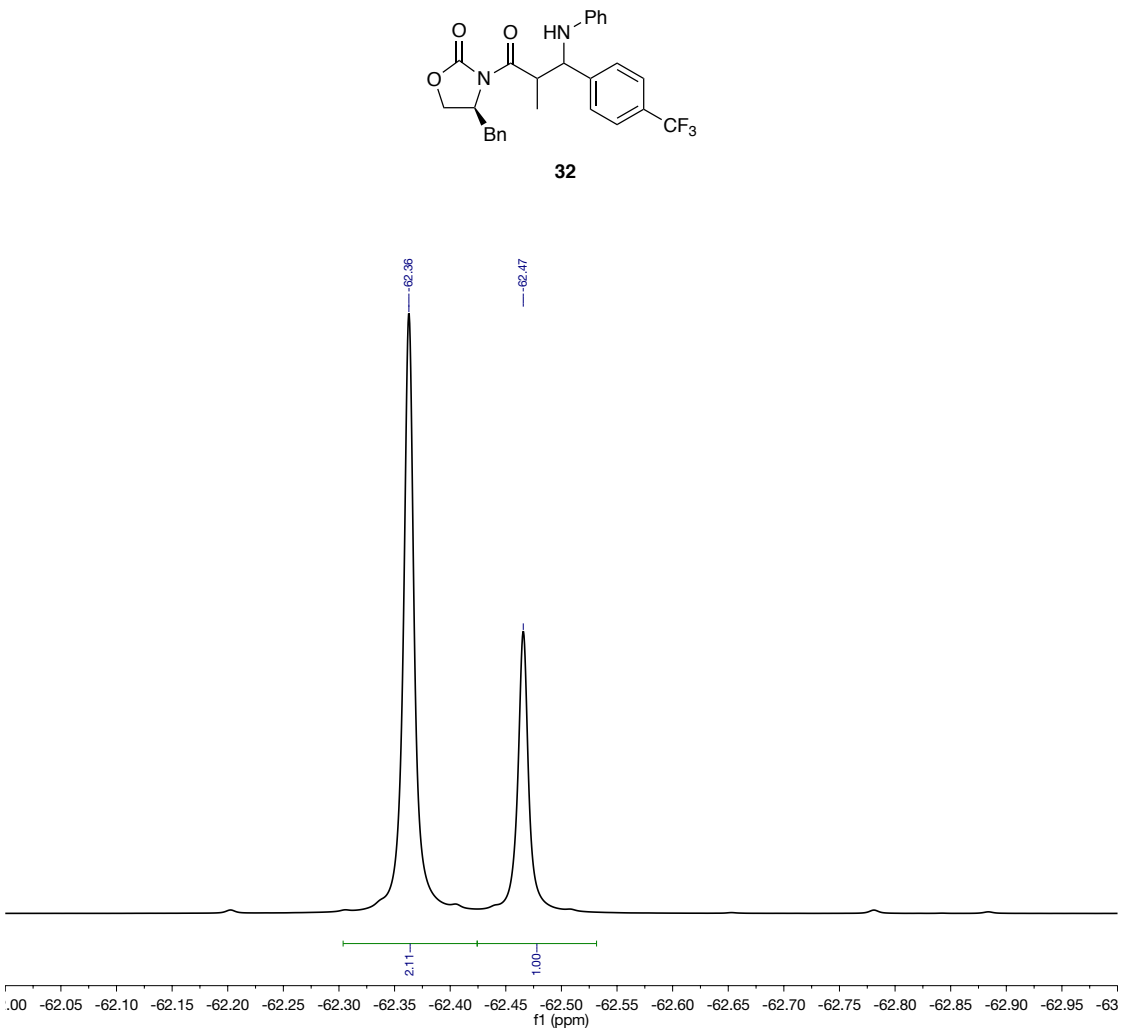
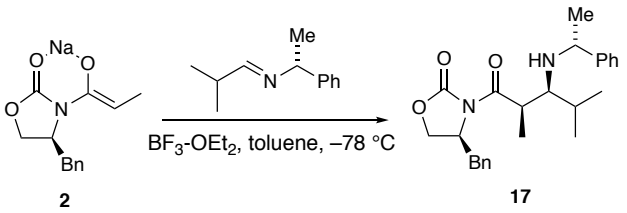


Figure A.2.136. ^{19}F NMR spectrum ($CDCl_3$, 25 °C) of **32**. Integration provides a selectivity of 2:1.



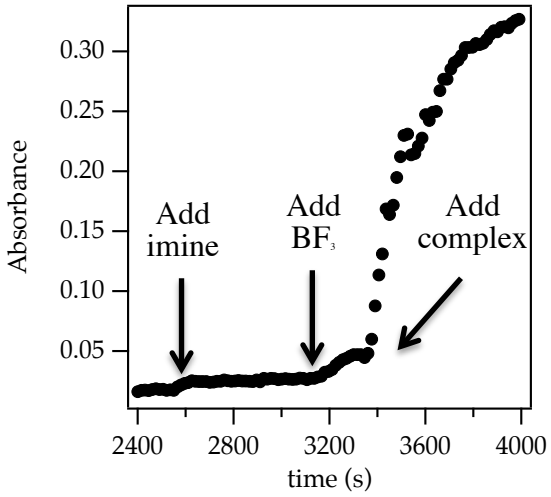
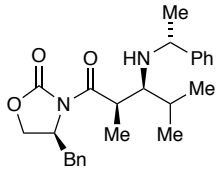


Figure A.2.137. IR spectra following auxiliary C=O peak in a solution of 0.20 M **2** in 0.40 M TMEDA/toluene with sequential addition of 0.20 M imine, 0.20 M BF_3□OEt_2 and 0.20 M **20** recorded at –78 °C.
Aza-aldol reaction requires the imine and BF_3 to be precomplexed. Adding imine and BF_3 separately does not work. Only adding the pre-formed complex works.

(4*S*)-4-benzyl-3-(2,4-dimethyl-3-(((*R*)-1-phenylethyl)amino)pentanoyl)oxazolidin-2-one (**17**). To a solution of NaHMDS (0.11 mmol, 20.2 mg) and TMEDA (0.22 mmol, 33 μL) in toluene (2.0 mL), **1** (0.10 mmol, 23.3 mg) was added. The reaction was stirred under Ar for 30 minutes at –78 °C. A solution of imine-BF_3 complex **20** (0.10 mmol) in toluene (0.20 mL) was injected and the mixture was stirred for 30 minutes. The reaction was quenched by 1.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N) afforded **17** in >30:1 selectivity and 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.24 (m, 3H), 7.22 – 7.16 (m, 3H), 4.63 (ddt, *J* = 10.8, 7.3, 3.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.09 (dd, *J* = 9.1, 3.4 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.25 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.87 (dd, *J* = 6.7, 4.2 Hz, 1H), 2.52 (dd, *J* = 13.2, 10.3 Hz, 1H), 1.80 (pd, *J* = 6.9, 4.2 Hz, 1H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.23, 153.22, 146.33, 135.63, 129.48, 129.09, 128.42, 127.43, 127.16, 127.00, 66.04, 60.80, 56.84, 55.53, 40.84, 38.16, 31.84, 24.32, 20.67, 18.09, 14.15. m/z calculated for $(M+H)^+$ 409.24857, found 409.24796.



17

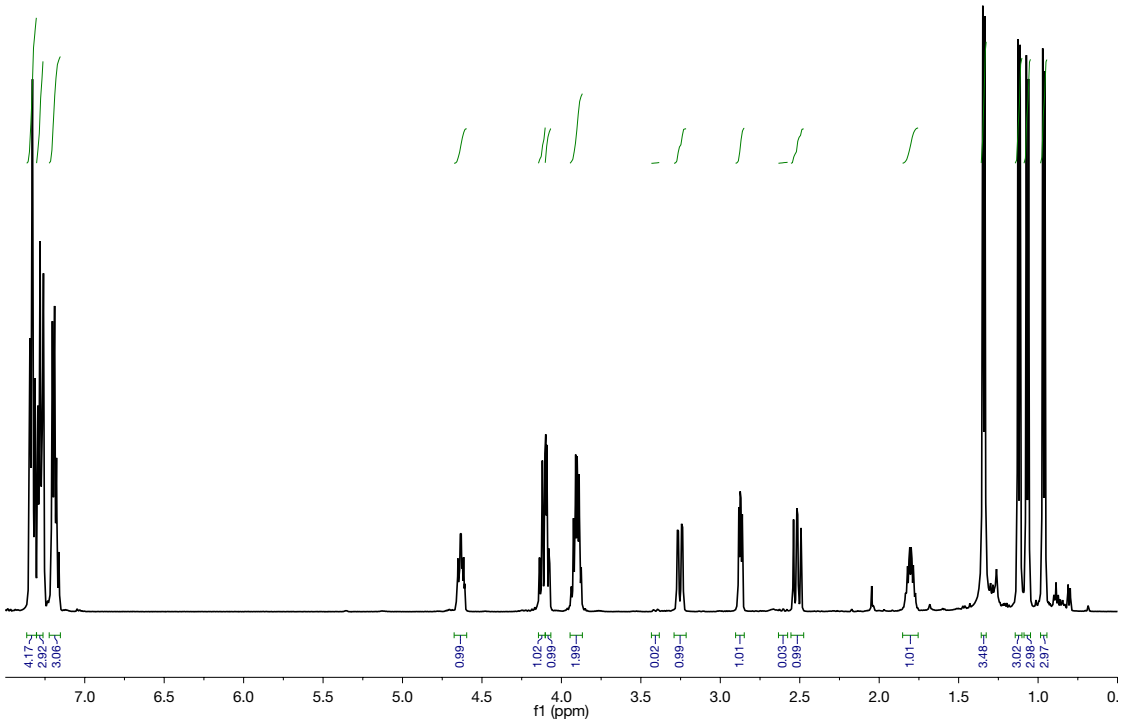


Figure A.2.138. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **17**.

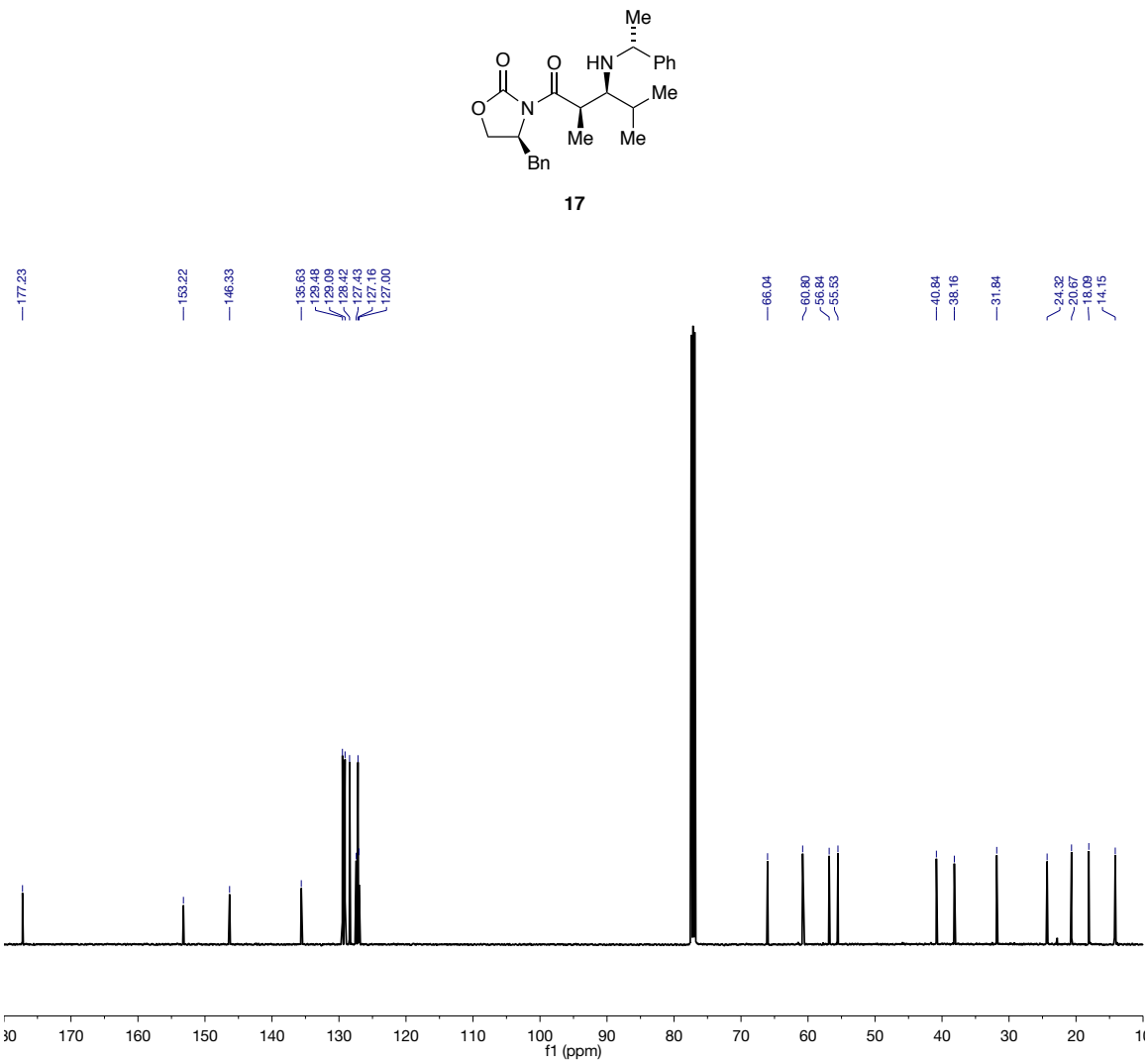
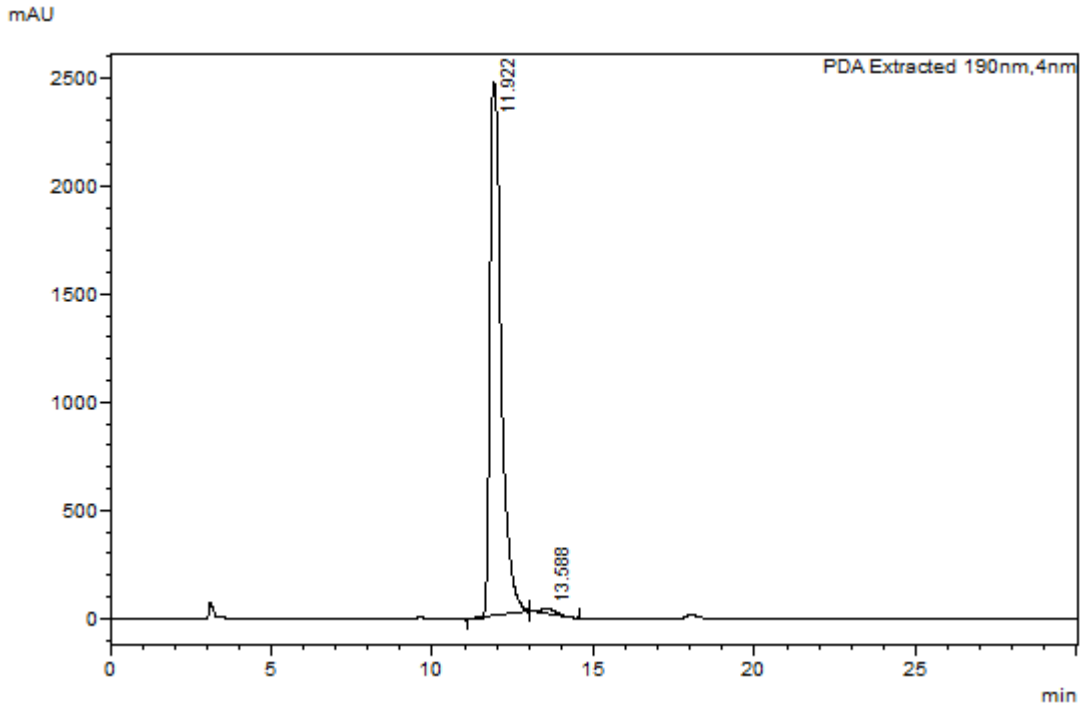


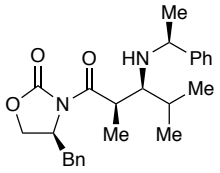
Figure A.2.139. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **17**.



Peak#	Ref. Time	Area	Height	Area%
1	11.922	60192867	2465748	98.89
2	13.588	675348	20705	1.11
Total		60868215	2486453	100

Figure A.2.140. HPLC spectrum of **17** in *i*-PrOH using OD column and 5% *i*-PrOH/hexane.

(4*S*)-4-benzyl-3-(2,4-dimethyl-3-(((*S*)-1-phenylethyl)amino)pentanoyl)oxazolidin-2-one (**16**). To a solution of NaHMDS (1.0 mmol, 183 mg) and TMEDA (2.0 mmol, 300 μL) in toluene (4.5 mL) was added **1** (1.0 mmol, 233 mg) followed by stirring under argon for 30 minutes at –78 °C. A solution of imine-BF_3 complex **19** (1.0 mmol) in toluene (0.20 mL) was injected. After stirring for 30 m, the reaction was quenched by 5.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude product showed **16** in >30:1 selectivity using ^{1}H NMR spectroscopy. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N) afforded **16** (380 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 7.6, 2.8 Hz, 4H), 7.31 – 7.25 (m, 3H), 7.25 – 7.19 (m, 3H), 4.70 (ddt, *J* = 10.9, 7.2, 3.4 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.15 – 4.11 (m, 1H), 3.95 (p, *J* = 6.8 Hz, 1H), 3.86 (q, *J* = 6.5 Hz, 1H), 3.40 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.88 (dd, *J* = 6.2, 4.8 Hz, 1H), 2.60 (dd, *J* = 13.1, 10.4 Hz, 1H), 1.67 (pd, *J* = 6.9, 4.9 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.35, 153.32, 146.49, 135.64, 129.48, 129.13, 128.37, 127.46, 127.27, 127.02, 66.17, 61.44, 57.74, 55.71, 41.64, 38.38, 32.49, 24.25, 20.74, 17.86, 13.82. m/z calculated for $(M+H)^+$ 409.24857, found 409.24889.



16

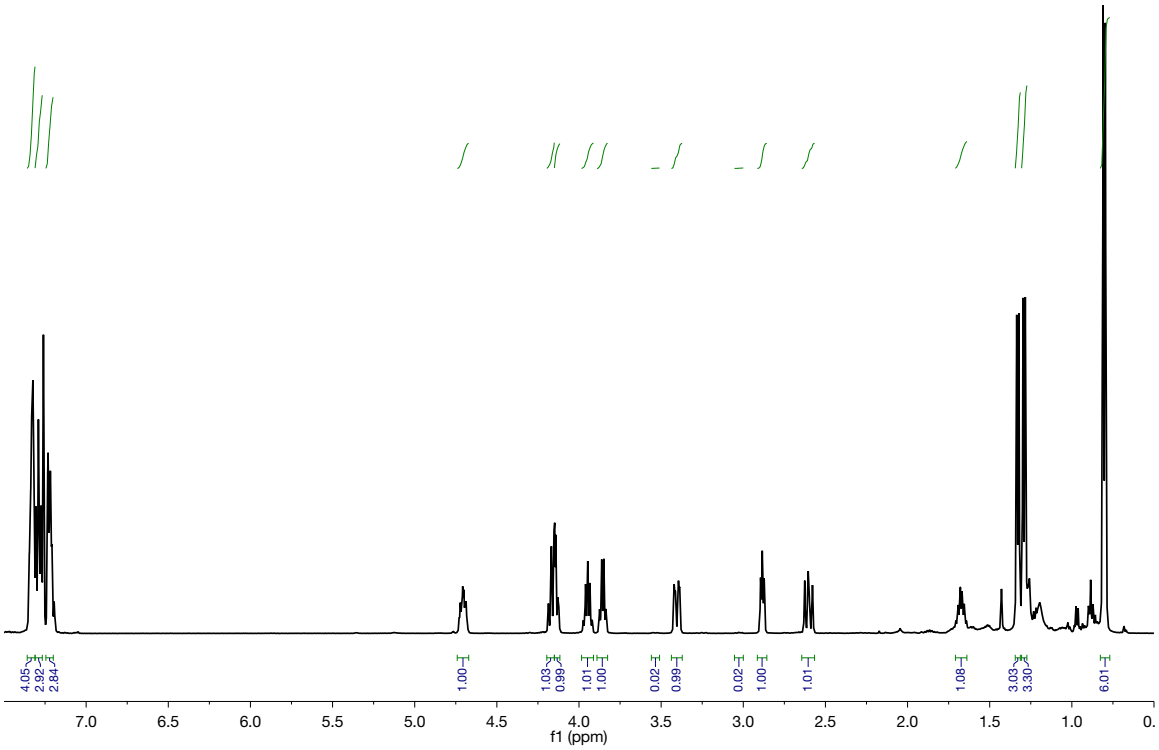


Figure A.2.141. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **16**.

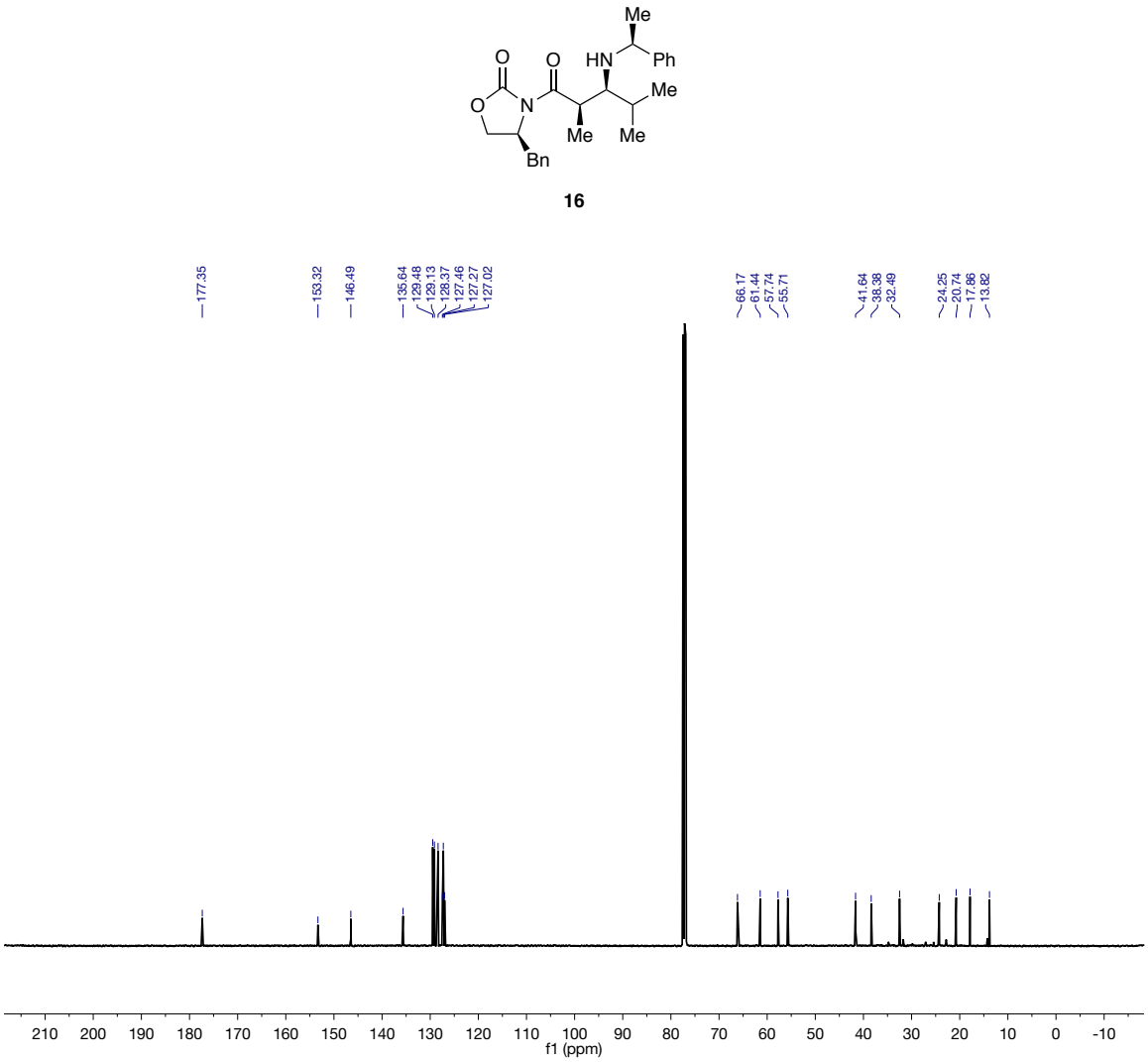


Figure A.2.142. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **16**.

(4*S*)-3-(3-amino-2,4-dimethylpentanoyl)-4-benzyloxazolidin-2-one (**22**). To a solution of **17** (0.08 mmol, 33.3 mg) in methanol (2 mL) was added palladium on carbon (0.008 mmol, 8.5 mg). Reaction was stirred under 1.0 atm of H_2 for 24 hr at room temperature. After filtering through Celite and concentrating in vacuo, flash chromatography with 3% triethylamine in ethyl acetate afforded **22** (14.5 mg, 60% yield). ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.26 – 7.25 (m, 1H), 7.25 – 7.20 (m, 3H), 7.20 – 7.16 (m, 1H), 5.17 – 5.05 (m, 2H), 4.02 – 3.95 (m, 1H), 3.83 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.24 (dd, *J* = 13.7, 9.7 Hz, 1H), 3.12 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.66 (p, *J* = 7.0 Hz, 1H), 1.64 (pd, *J* = 14.0, 6.9 Hz, 1H), 0.97 – 0.87 (m, 3H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.32, 155.43, 138.18, 129.51, 128.49, 126.62, 63.85, 60.55, 55.92, 34.67, 27.90, 18.77, 18.18, 9.89. m/z calculated for $(M+H)^+$ 305.18597, found 305.18521.

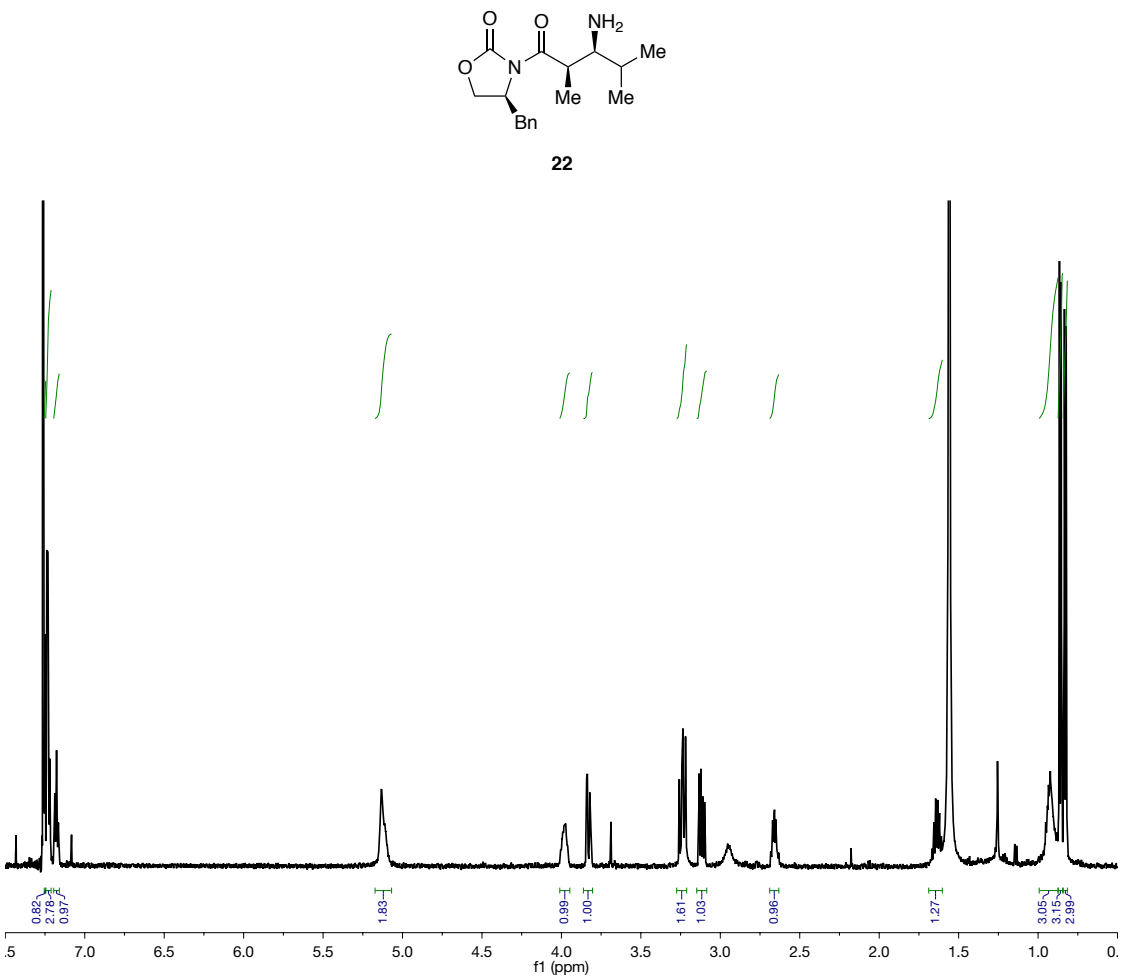
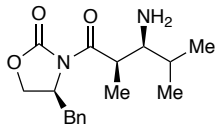


Figure A.2.143. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **22**.



22

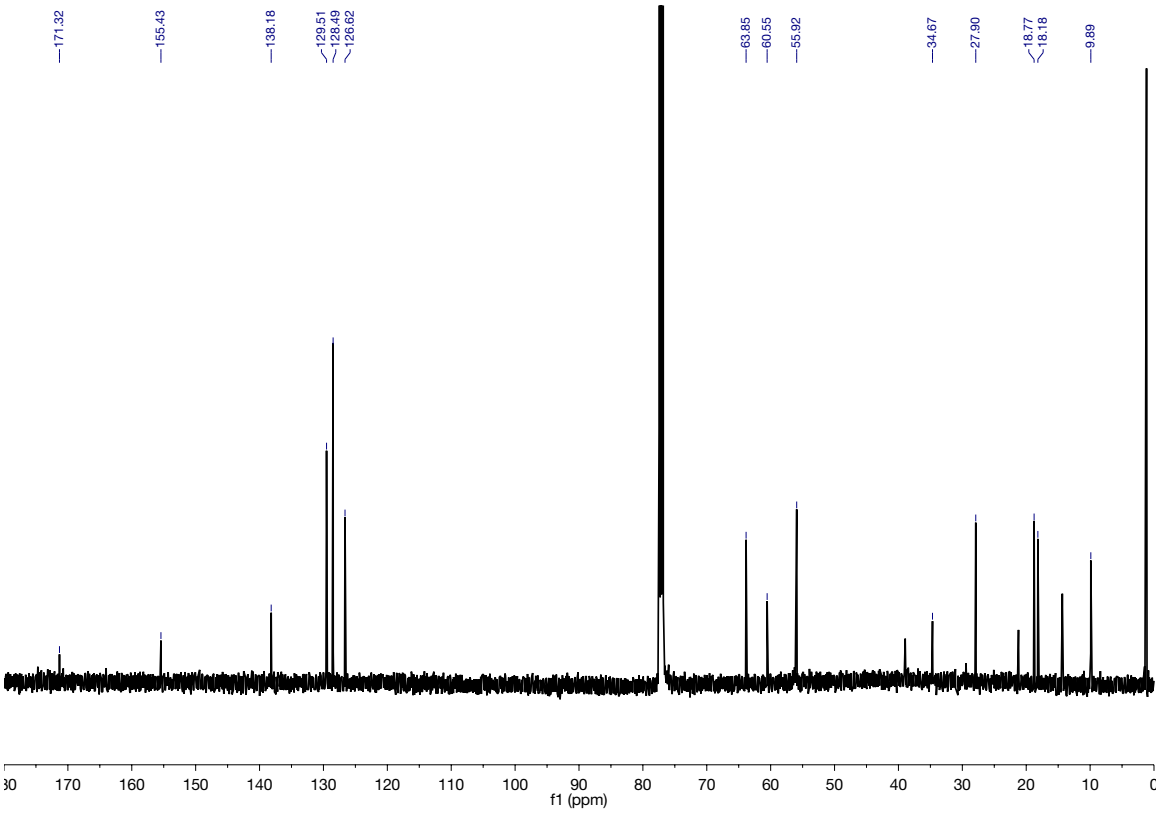


Figure A.2.144. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **22**.

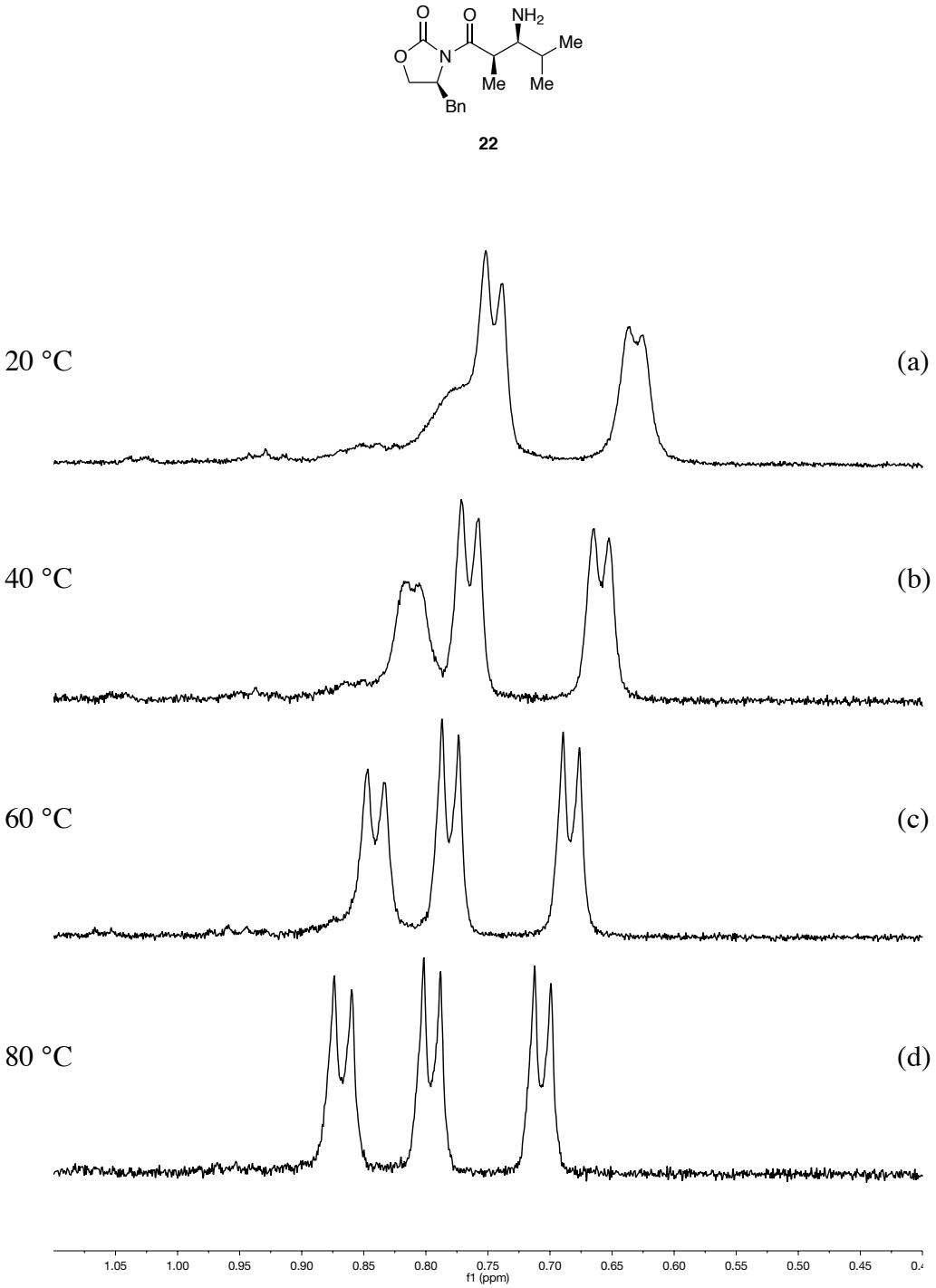


Figure A.2.145. ^{1}H NMR spectrum of **22** in DMSO-d_6 recorded at (a) 20 °C; (b) 40 °C; (c) 60°C; (d) 80 °C.

(4*S*)-4-benzyl-3-(3-(benzylamino)-2,4-dimethylpentanoyl)oxazolidin-2-one (**18**). To a solution of NaHMDS (0.11 mmol, 20.2 mg) and TMEDA (0.22 mmol, 33 μL) in toluene (2.0 mL), **1** (0.10 mmol, 23.3 mg) was added. Reaction was stirred under argon for 30 minutes at –78 °C. A solution of imine-BF_3 complex **21** (0.10 mmol) in toluene (0.20 mL) was injected and the mixture was stirred for 30 minutes. The reaction was quenched by 1.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N afforded **18** (34.3 mg, 87% yield), shown by ^1H NMR to be **18** and its minor diastereomer in 17:1 selectivity. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 7.24 – 7.21 (m, 3H), 4.73 (ddt, *J* = 11.0, 7.3, 3.5 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.14 (dd, *J* = 9.1, 3.6 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.86 (d, *J* = 12.5 Hz, 1H), 3.81 (d, *J* = 12.5 Hz, 1H), 3.40 (dd, *J* = 13.2, 3.4 Hz, 1H), 2.90 (t, *J* = 6.0 Hz, 1H), 2.60 (dd, *J* = 13.1, 10.4 Hz, 1H), 1.81 (pd, *J* = 13.3, 6.7 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.99, 153.30, 141.05, 135.60, 129.43, 129.09, 128.46, 128.28, 127.42, 127.06, 66.20, 64.67, 55.57, 55.30, 41.14, 38.33, 32.33, 20.42, 18.83, 12.57. m/z calculated for $(M+H)^+$ 395.23292, found 395.23215.

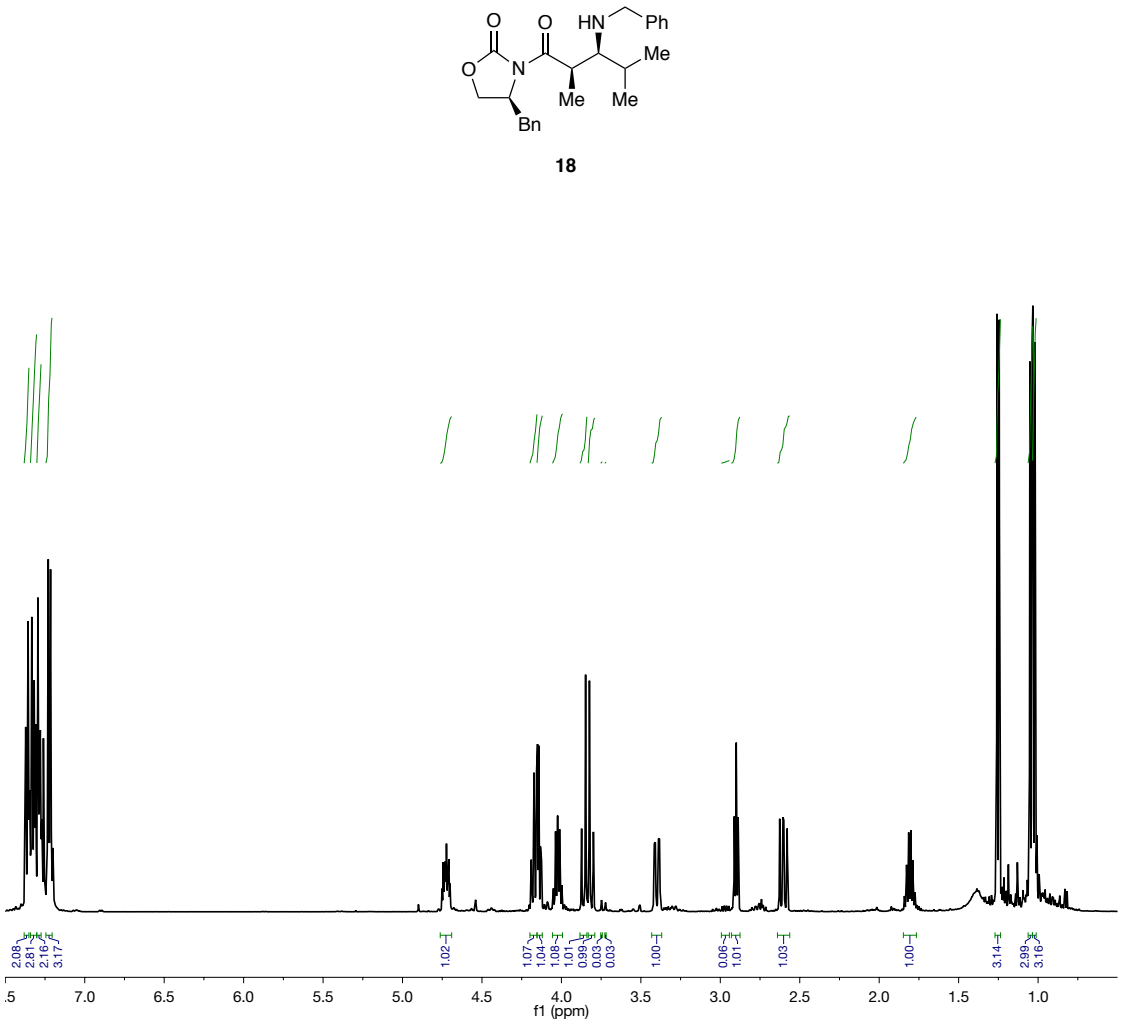
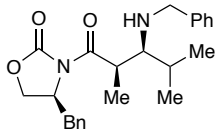


Figure A.2.146. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **18**.



18

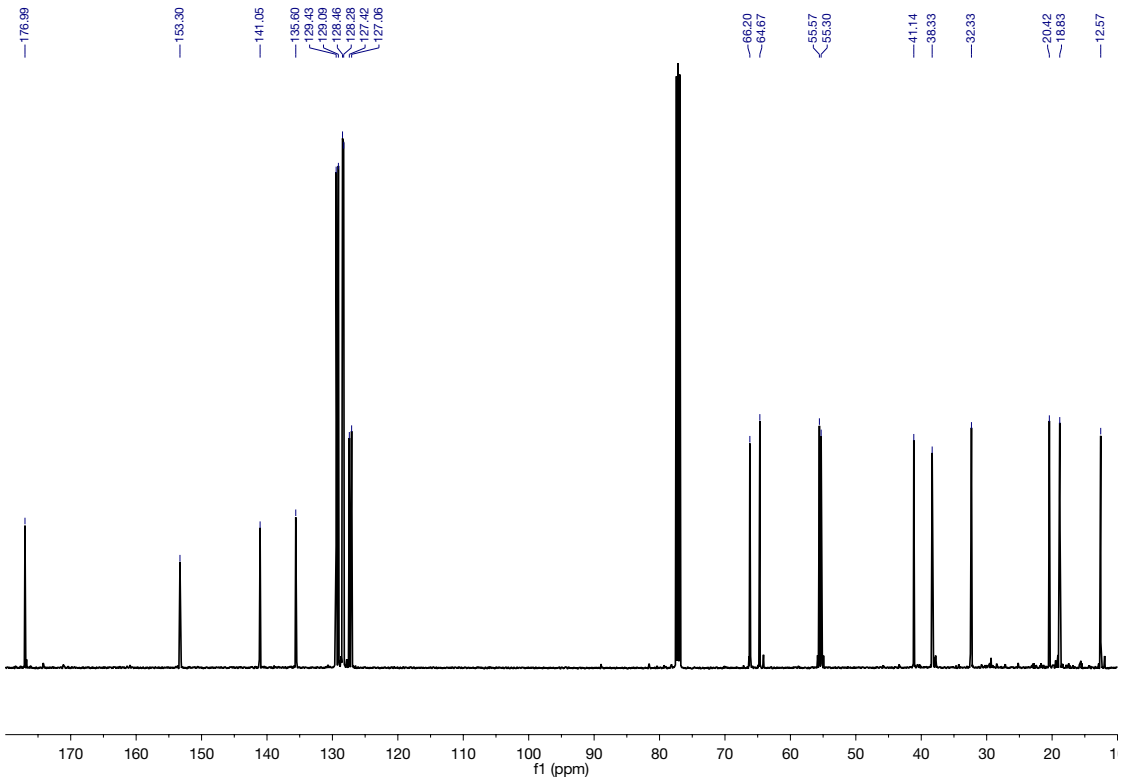


Figure A.2.147. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **18**.

(2*R*, 3*S*)-3-((*tert*-butoxycarbonyl)amino)-2,4-dimethylpentanoate (**37**). To a solution of **18** (1.3 mmol, 500 mg) in methanol (5.0 mL), sodium methoxide (1.3 mmol, 70 mg) was added. The mixture was stirred for 30 minutes at 0 °C. The reaction was quenched by 1.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes afforded the methyl ester (57.8 mg, 18% yield). The methyl ester in THF (1.0 mL) was added to palladium on carbon (6.0 mg) and stirred under H_2 (1.0 atm) for 24 hrs. The mixture was filtered through celite and used in the next step without further purification. To the primary amine in THF, di-tert-butyl dicarbonate (0.30 mmol, 218 mg), triethyl amine (1.0 mmol, 139 μL), and 4-dimethylaminopyridine (0.020 mmol, 2.4 mg) were added. The reaction was stirred at room temperature for 8 hrs and concentrated in vacuo. Flash chromatography (15% ethyl acetate/hexanes) afforded the product (8.8 mg, 15%) shown by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 (d, *J* = 10.6 Hz, 1H), 3.78 (dt, *J* = 10.7, 6.6 Hz, 1H), 3.67 (s, 3H), 2.62 (p, *J* = 7.0 Hz, 1H), 1.66 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.46 (s, 1H), 1.42 (s, 8H), 1.12 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.47, 155.97, 79.29, 57.53, 51.90, 42.36, 30.51, 28.48, 20.32, 17.67, 12.31. m/z calculated for $(M+H)^+$ 260.18563, found 260.18518. $[\alpha]^{22} = -11$, c 0.40, $CDCl_3$. Literature reported $[\alpha]^{22} = -16.3$, c 1.0, $CHCl_3$.

Seebach, D.; Abele, S.; Gademann, K.; Guichard, G.; Hintermann, T.; Jaun, B.; Matthews, J. L.; Schreiber, J. V. *Helvetica Chimica Acta,* **1998**, *81*, 932.

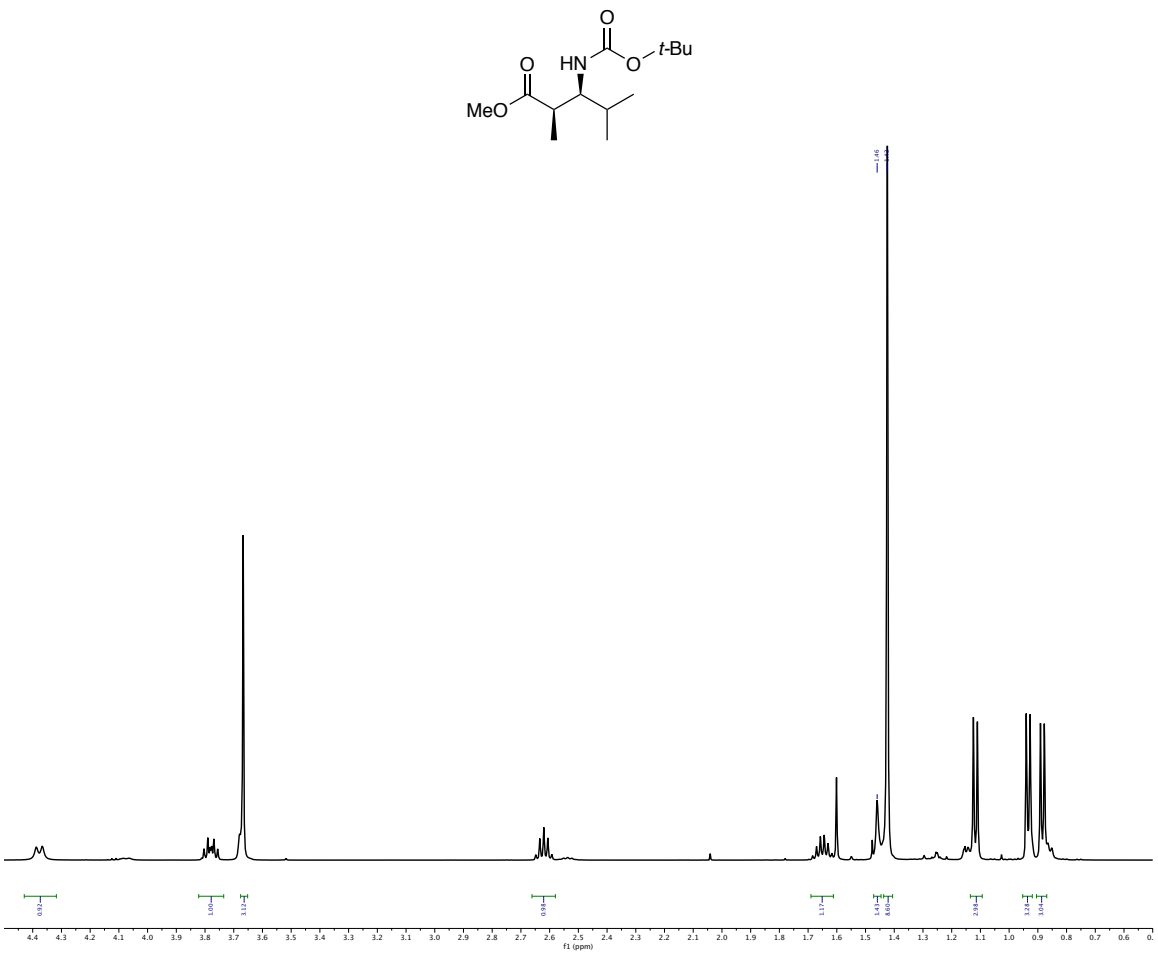


Figure A.2.148. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **37**.

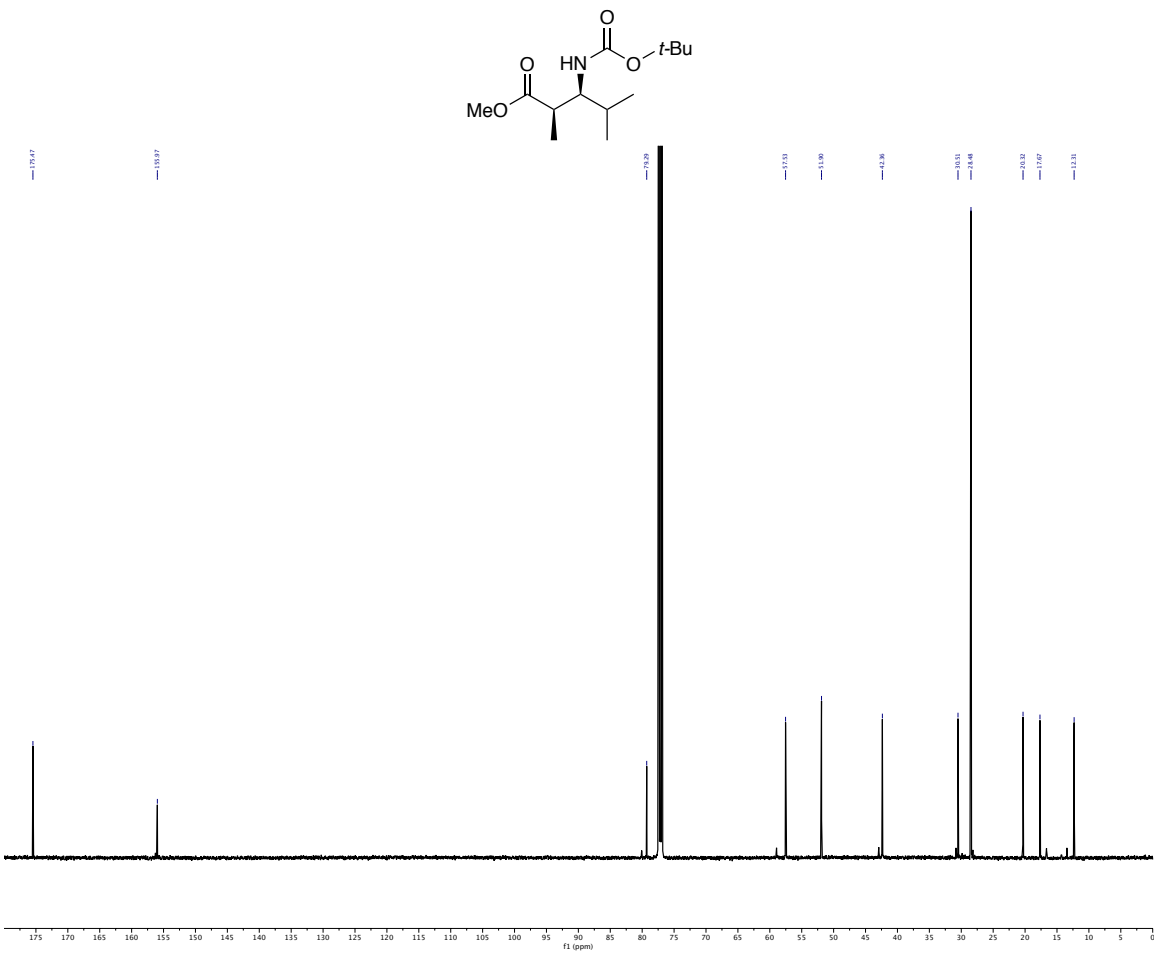


Figure A.2.149. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **37**.

(4*S*)-4-benzyl-3-(4-methyl-3-(((*R*)-1-phenylethyl)amino)pentanoyl)oxazolidin-2-one (**33**). To a solution of NaHMDS (0.11 mmol, 20.2 mg) and TMEDA (0.22 mmol, 33 μL) in toluene (2.0 mL) was added **1** (0.10 mmol, 23.3 mg). The reaction was stirred under argon for 30 minutes at –78 °C. A solution of imine-BF_3 complex **20** (0.10 mmol) in toluene (0.20 mL) was injecte, and the mixture was stirred for 30 minutes. The reaction was quenched by 1.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N) afforded the product (33 mg, 84% yield), shown by ^{1}H NMR to be **33** in 1.2:1 selectivity. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 5H), 7.23 – 7.16 (m, 3H), 4.61 (ddt, *J* = 10.4, 7.0, 3.5 Hz, 1H), 4.15 – 4.11 (m, 1H), 4.11 – 4.08 (m, 1H), 3.87 (q, *J* = 6.6 Hz, 1H), 3.27 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.03 – 2.96 (m, 1H), 2.96 – 2.92 (m, 1H), 2.83 (dd, *J* = 13.8, 2.7 Hz, 1H), 2.64 (dd, *J* = 13.4, 9.9 Hz, 1H), 2.01 (dtt, *J* = 10.3, 6.9, 3.5 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.10, 153.70, 146.13, 135.61, 129.56, 129.09, 128.40, 127.44, 126.88, 126.83, 66.14, 56.96, 55.38, 54.98, 38.16, 36.23, 29.35, 25.50, 19.19, 16.47.

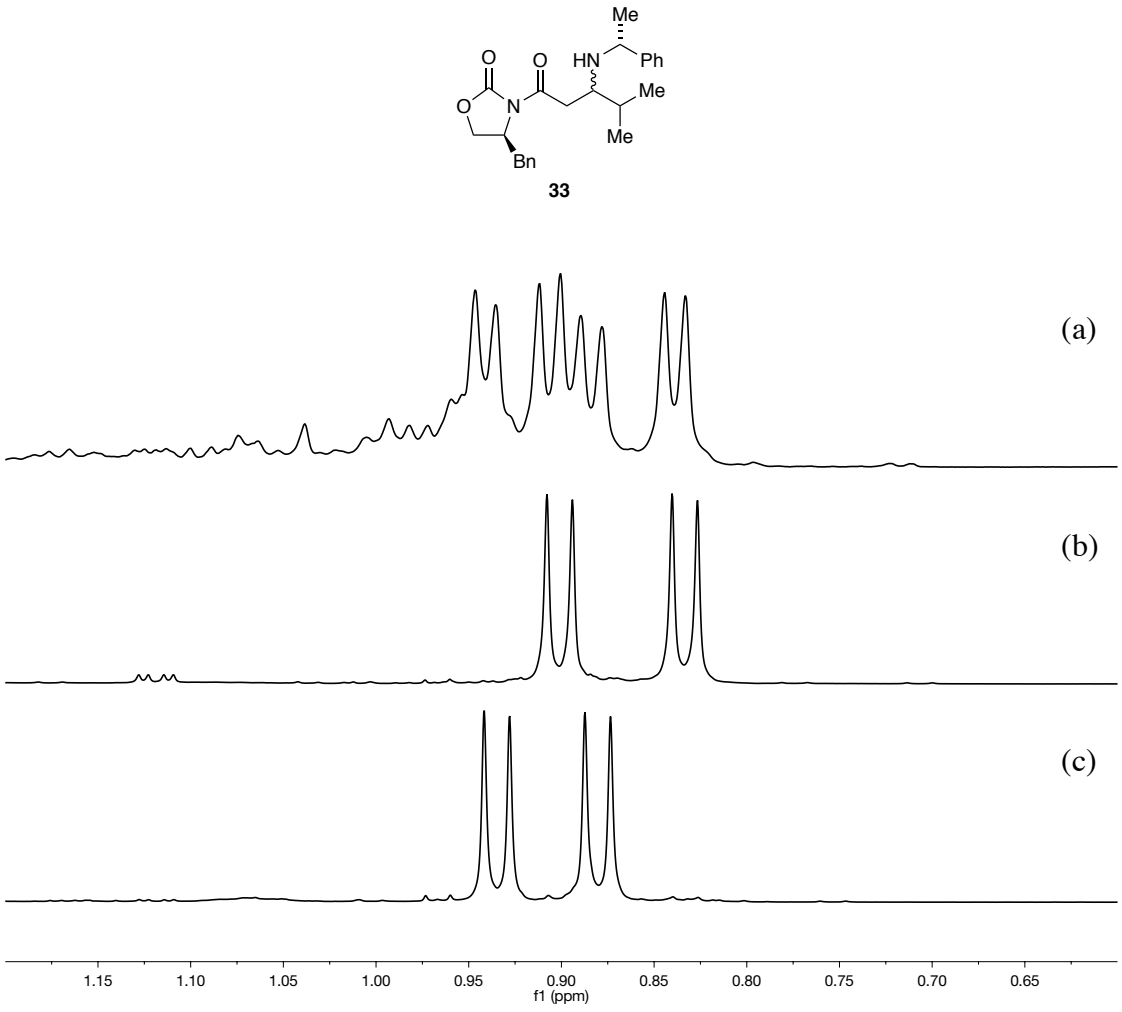


Figure A.2.150. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (a) **33**; (b) isomer A, and (c) isomer B.

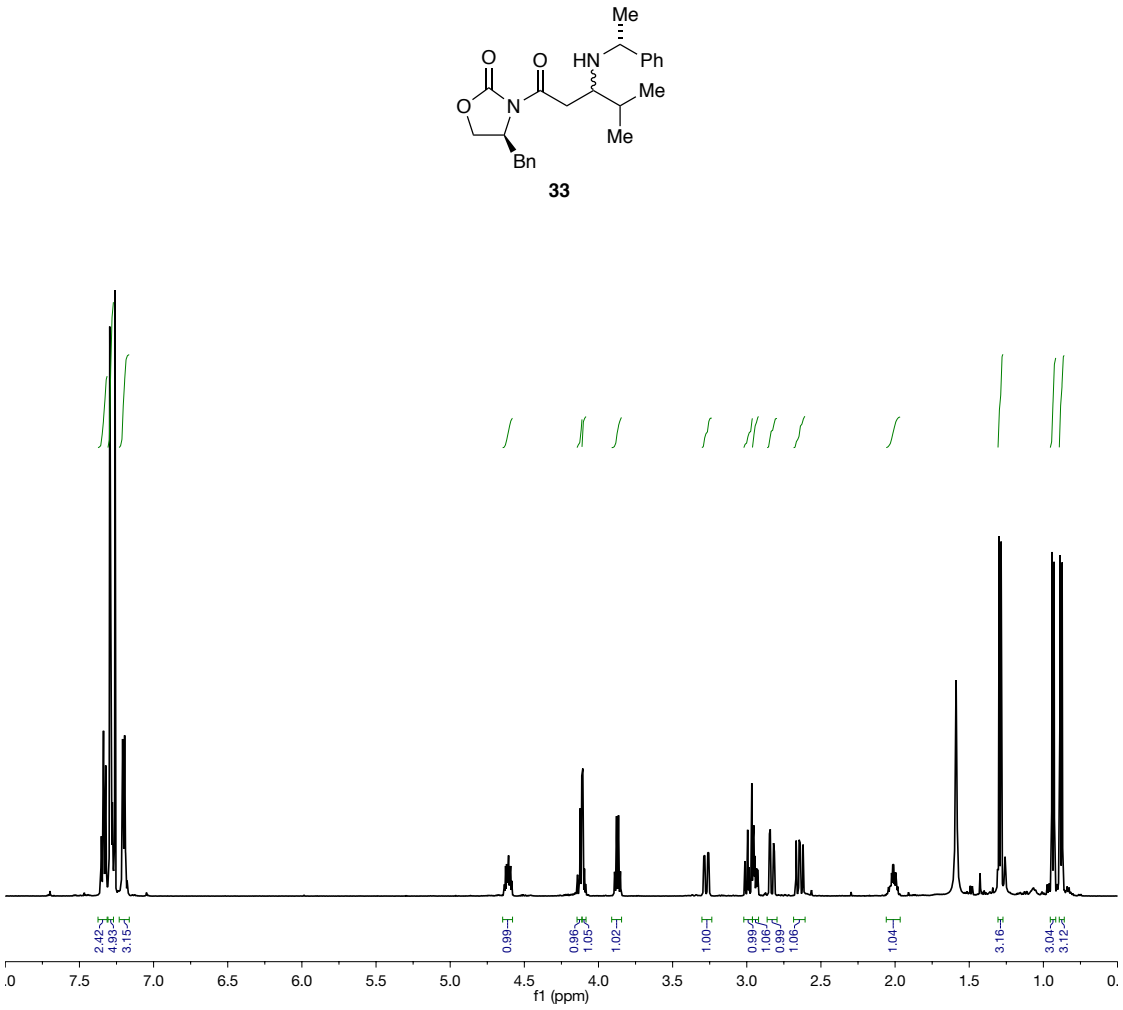
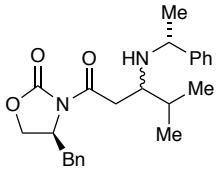


Figure A.2.151. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **33**.



33

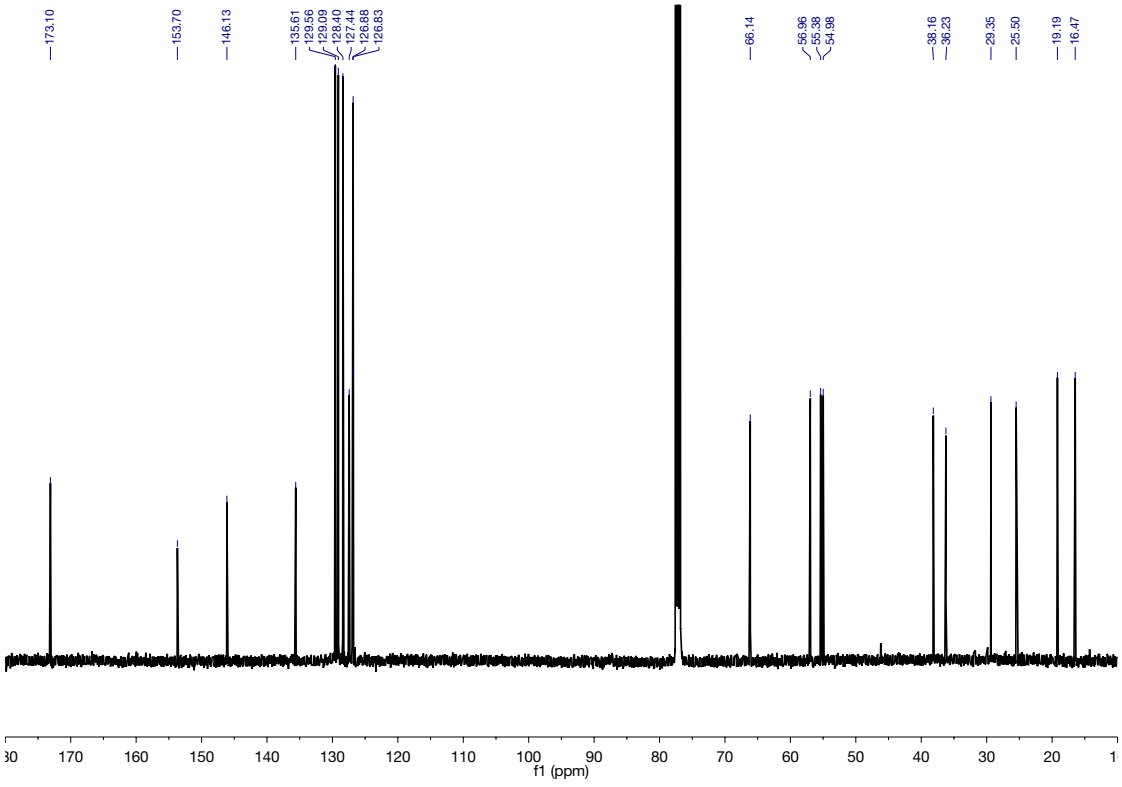


Figure A.2.152. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **33**.

(4*S*)-4-benzyl-3-(4-methyl-3-(((*S*)-1-phenylethyl)amino)pentanoyl)oxazolidin-2-one (**34**). To a solution of NaHMDS (0.11 mmol, 20.2 mg) and TMEDA (0.22 mmol, 33 μL) in toluene (2.0 mL) was added **1** (0.10 mmol, 23.3 mg). The reaction was stirred under argon for 30 minutes at –78 °C. A solution of imine-BF_3 complex **19** (0.10 mmol) in toluene (0.20 mL) was injected, and the mixture was stirred for 30 minutes. The reaction was quenched by 1.0 mL saturated NH_4Cl and extracted three times with EtOAc. The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (10% ethyl acetate/hexanes/3% Et_3N) afforded **34** (33.4 mg, 85% yield) as a 1:1 mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 5H), 7.26 – 7.23 (m, 2H), 7.20 – 7.15 (m, 1H), 4.53 (dddd, *J* = 9.8, 7.6, 3.4, 2.3 Hz, 1H), 4.07 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.97 (ddd, *J* = 8.7, 7.6, 0.8 Hz, 1H), 3.86 (q, *J* = 6.6 Hz, 1H), 3.34 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.95 – 2.91 (m, 1H), 2.87 – 2.77 (m, 2H), 2.74 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.04 (ddh, *J* = 10.1, 6.9, 3.1 Hz, 1H), 1.31 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.02, 153.53, 146.14, 135.68, 129.62, 129.10, 128.31, 127.43, 126.99, 126.88, 65.99, 56.91, 55.56, 54.88, 37.87, 36.47, 29.19, 25.36, 19.25, 16.31.

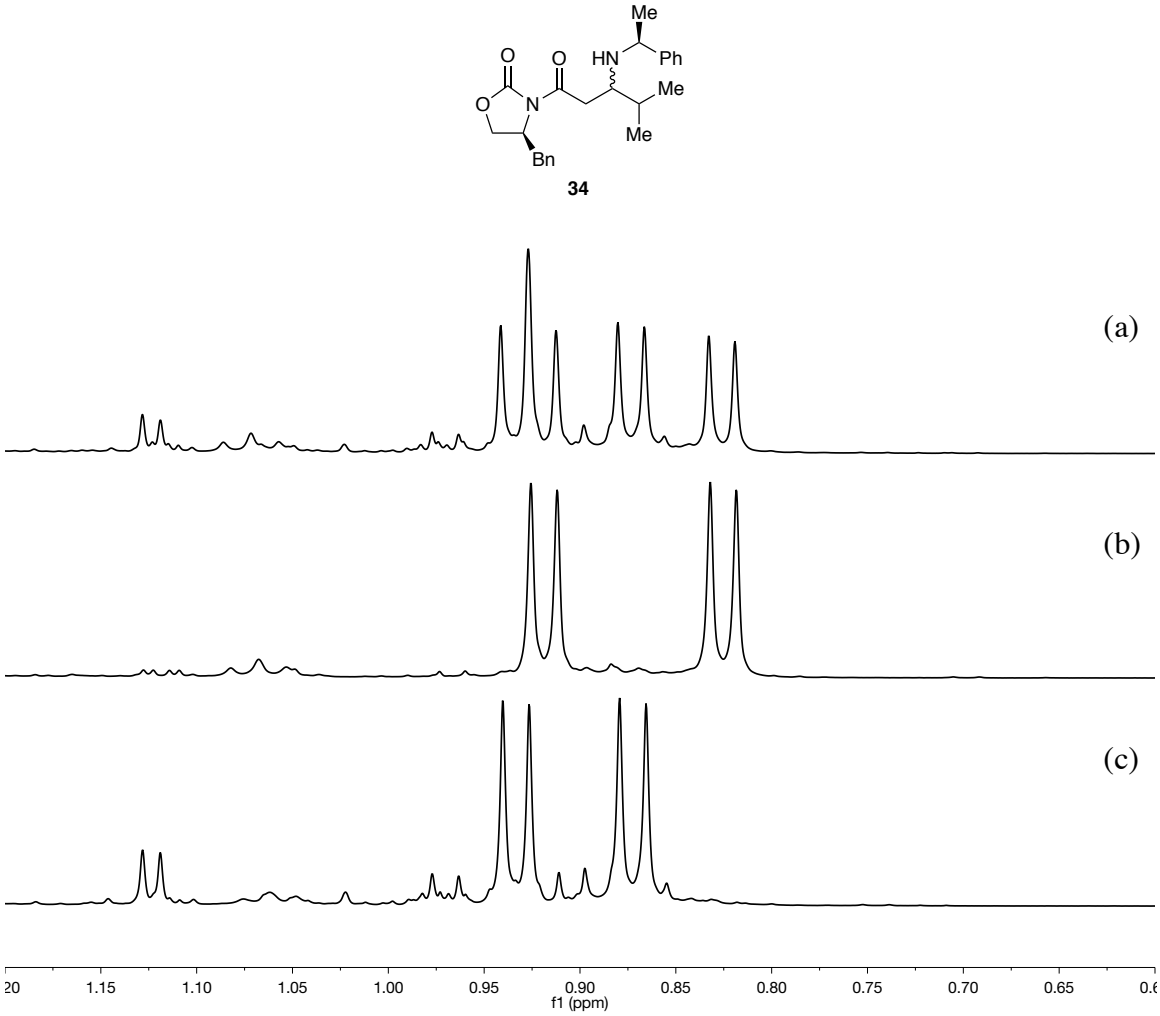


Figure A.2.153. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of (a) **34**; (b) isomer A, and (c) isomer B.

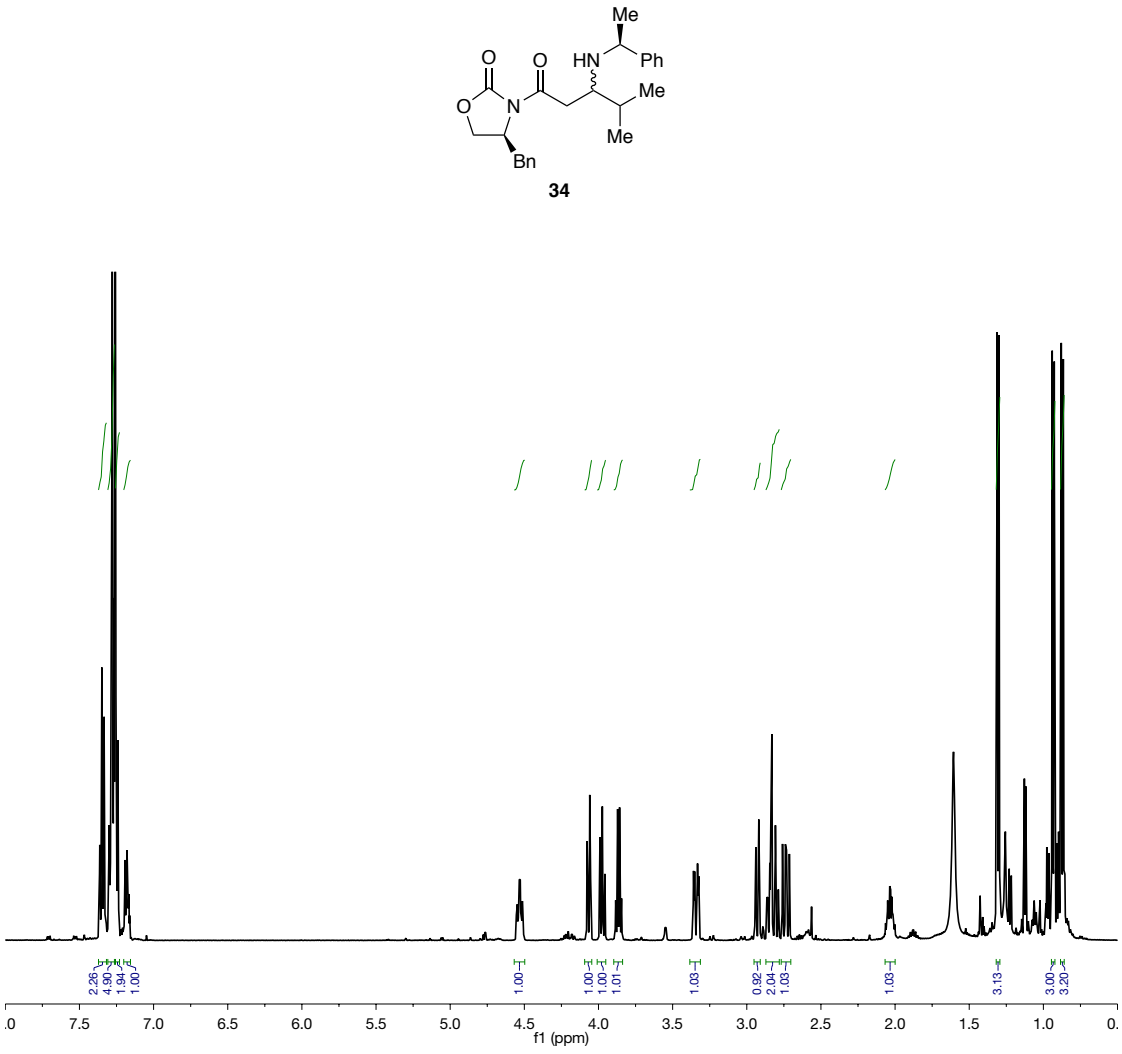


Figure A.2.154. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of **34**.

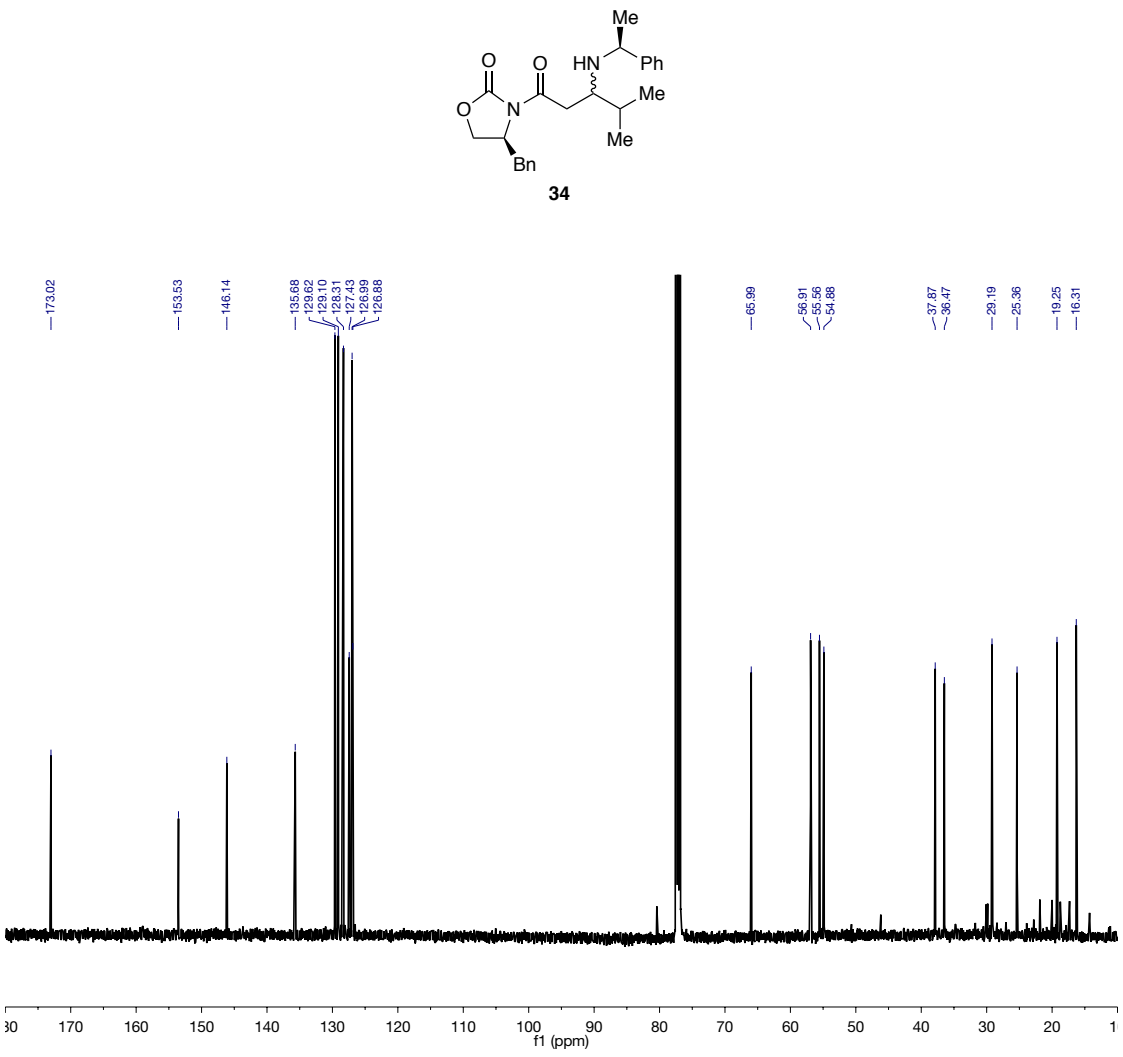


Figure A.2.155. ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of **34**.

$$K_{eq}(1) = \frac{[LL'][L]}{[L_2][L']}$$
$$K_{eq}(2) = \frac{[L'_2][L]}{[LL'][L']}$$

The distributions of homo- and heterosolvated enolate disolvated monomers are assumed to track as power functions of the L and L' mole fractions. While the fit is superficially similar to that described previously for two subunits aggregating to form one or more ensembles, we substitute the measured mole fraction for the total mole fraction of solvent and consequently obviate parametric fitting. Accordingly,

$$[L_2] = c\Phi_0(1-\chi_{L'})^2$$
$$[LL'] = 2c\Phi_1(1-\chi_{L'})\chi_{L'}$$
$$[L'_2] = c\Phi_2{\chi_{L'}}^2$$

The c prefactor subsumes the concentration units and normalization such that $[enolate]_{total} = [L_2] + [LL'] + [L'_2]$. Therefore,

$$c = \frac{[enolate]}{\Phi_0(1-\chi_{L'})^2 + 2\Phi_1(1-\chi_{L'})\chi_{L'} + \Phi_2{\chi_{L'}}^2}$$

We wish to compute each of the equilibrium constants defined above and do so by substituting in the fitting functions for each homo- and heterosolvate,

$$K_{e\square}(1) = \frac{[LL'][L]}{[L_2][L']} = \frac{2c\Phi_1(1-\chi_{L'})\chi_{L'}[L]}{c\Phi_0(1-\chi_{L'})^2[L']} = \frac{2\Phi_1\chi_{L'}[L]}{\Phi_0(1-\chi_{L'})[L']}$$
$$K_{eq}(2) = \frac{\Phi_2\chi_{L'}[L]}{2\Phi_1(1-\chi_{L'})[L']}$$

Assuming the absence of unsolvated enolate tetramers, one can compute the normalities of all species and thereby extract the equilibrium constants point-wise from the data employing the equations described above.

L = TMEDA, L’ = (*S*,*S*)-TMCDA

Normalities of homo- and heterosolvated enolate tetramers corresponding to computed molarities of free solvent

$[L_2]$	[LL']	$[L'_2]$	[L]	[L']
0.200	0	0	0.600	0
0.166	0.034	0	0.434	0.166
0.106	0.089	0.005	0.299	0.301
0.058	0.095	0.047	0.189	0.411
0.037	0.101	0.062	0.125	0.475
0.017	0.079	0.104	0.087	0.513
0	0.050	0.150	0.050	0.550
0	0	0.200	0	0.600

Computed equilibrium constants

K(1)	*K*(2)
-	-
0.525	-
0.831	0.060
0.756	0.225
0.729	0.161
0.812	0.224
-	0.268
-	-

Averaging the computed equilibrium constants gives $K(1) = 0.782$, $K(2) = 0.220$.

The data from the Job plot experiments can be fit parametrically to a mathematical model for a specific ensemble. The programs for performing these fits were written for use in MATLAB_R2018a.

Data1.m

```
XA = [1
0.8
0.6
0.4
0.3
0.2
0.1
0];

Expt_Populations =[0    0   1
0   0.16    0.84
0.04    0.34    0.62
0.23    0.44    0.33
0.32    0.46    0.21
0.58    0.37    0.06
0.81    0.19    0
1   0   0;];

peak_assignment = [3  2  1];

phi = [ 1  1  1 ];

%To see your plot:  try_fit(XA, phi, peak_assignment, Expt_Populations)

%To fit your plot:  [phi_new, error] = refine_fit(XA, phi, peak_assignment,
Expt_Populations)

%or for symmetric plots:  [phi_new, error] = refine_fit_s(XA,phi,peak_assignment,
Expt_Populations)
```

Error of Model.m

```
function [mean_error, pop_error] = Error_of_Model(XA,phi, peak_assignment,
Expt_Populations, Expt_weights)

    if (nargin<5) % If no info on data given assume all points equally precise.
            Expt_weights=ones(size(Expt_Populations));
    end

    Concentrations = multimers(XA,phi);
    PP = Populations(Concentrations, peak_assignment);
    % Compute the mean error.
    diff = PP - Expt_Populations;
    mean_error = sqrt(sum(sum(diff.*diff.*Expt_weights)) / sum(sum(Expt_weights)));

    % Compute the error for each population independently.
    pop_error = sum(diff.*Expt_weights,1) ./ sum(Expt_weights,1);
    pop_error(2,:) = sqrt(sum(diff.*diff.*Expt_weights,1) ./ sum(Expt_weights,1));
```

multimers.m

```
function Concentration = multimer(XA, phi)

if (nargin<2)
   phi = [ 1 1 20 400 20 1 1];
end

for j=1:length(XA)
  % Use the function bisect to find Cconc
  Concentration(j,:) = bisect(XA(j),phi);
end

function Conc = bisect(XA, phi)

tolerance = 1e-6; % Amount XA may differ by an end of bisection..
   Amax = 1; Amin = 0;
   [Xmin, Conc]=Cparametric(Amin, phi);
   [Xmax, Conc]=Cparametric(Amax, phi);

   while ((Xmax-XA)>tolerance) % While not close enough, continue to bisect
difference of rmin and rmax.
      Atest = (Amin+Amax)/2;
      [Xtest, Conc]=Cparametric(Atest,phi);

      if (Xtest>XA)
         Amax = Atest; Xmax=Xtest;
      else
         Amin = Atest; Xmin=Xtest;
      end
  end

function [XA, Concs] = Cparametric( A, phi)

N = length(phi)-1;
B = 1-A;
Concs(1)= B^N*phi(1);
Concs(N+1)=A^N*phi(N+1);
Mn=1;

for k=2:N
   idx=k-1;
   Mn = Mn * (N+1-idx)/idx;
   Concs(k) = phi(k)*A^idx*B^(N-idx)*Mn;
end
```

Populations.m

```
function result = Populations(Concentrations, peak_assignment)

   result = zeros(size(Concentrations,1),max(peak_assignment));
   N = size(Concentrations,2);

   for j=1:N % Go through each type of aggregate and add to correct NMR peak.
      idx = peak_assignment(j);
      result(:,idx) = result(:,idx) + Concentrations(:,j);
   end
```

refine fit.m

```
function [phi_new, error] = refine_fit(XA,phi, peak_assignment, Expt_Populations)

if (nargin<5)
    Expt_weight = ones(size(Expt_Populations));
 end

N = length(phi)-1;
param = [ 2:(N+1)];

step_size = 0.1*phi(param),

N_no_progress = 0;
N_max_trials = 30;

[error_best, temp] = Error_of_Model(XA,phi, peak_assignment, Expt_Populations) ;
fprintf(1,'\n Initial Error of Fit = %f percent.\n', error_best * 100);

while (N_no_progress < N_max_trials)

   flag = 0;

   for k=1:length(param)

         phi_testr = phi;
         phi_testr(param(k))=abs(phi(param(k)) + step_size(k));
         [error_testr, temp] = Error_of_Model(XA,phi_testr, peak_assignment,
Expt_Populations, Expt_weight);
```

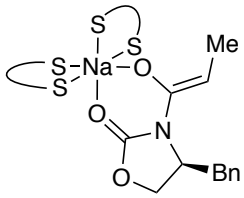
```
phi_testl = phi;
          phi_testl(param(k))=abs(phi(param(k)) - step_size(k));
          [error_testl, temp] = Error_of_Model(XA,phi_testl,
peak_assignment,Expt_Populations, Expt_weight);
.
        if (error_testr<error_best)
             error_best=error_testr; phi=phi_testr; step_size(k) = step_size(k) * 1.5;
             N_no_progress=0;
       elseif      (error_testl <error_best)
             error_best=error_testl; phi=phi_testl; step_size(k) = step_size(k) * 1.5;
             N_no_progress=0;
       else
          flag = flag + 1;
       end
   end

   if (flag>2)
      step_size = step_size * (0.75 + 0.25*rand);
      N_no_progress=N_no_progress+1;
   end

   fprintf(1,'\nError - %f , Last Good Step - %d , Mean Step Size - %f \n ',error_best,
N_no_progress, 100*mean(step_size./phi(param)));
   fprintf(1,' Phi - %f',phi);

   end

   error=error_best;
   phi_new = phi;
```

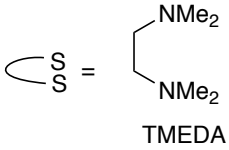
Try fit.m

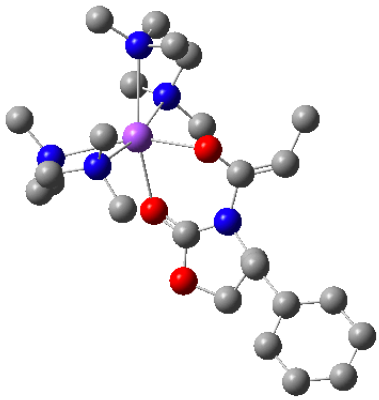
```
function try_fit(XA, phi, peak_assignment, Expt_Populations)

if (nargin<5)
            Expt_weights=ones(size(Expt_Populations));
   else
            Expt_weights = 1./( Expt_Errors + mean(mean(Expt_Errors)));
   end

hold on ; cscheme='bgrmkcybgrmkcy'; axis([0 1 0 1]); xlabel('X_A'); ylabel('Mole
Fractions');
     for j=1:size(Expt_Populations,2)
          if (nargin<5)
             plot(XA, Expt_Populations(:,j),sprintf('%so',cscheme(j)));
          else
             errorbar(XA, Expt_Populations(:,j),
Expt_Errors(:,j),sprintf('%so',cscheme(j)));
          end
     end

XAc = [0:0.01:1]; TP=Populations(multimers(XAc,phi), peak_assignment);
     for j=1:size(TP,2)
        plot(XAc,TP(:,j),sprintf('%c',cscheme(j)) );
     end

[mean_error, pop_error] = Error_of_Model(XA,phi, peak_assignment,
Expt_Populations, Expt_weights);
   N = length(phi)-1;
          fprintf(1,'\nThe Mean mismatch is %f peAcent.\n', mean_error*100);
          for j=1:size(pop_error,2)
          fprintf(1,'Predicted value of species A%dB%d +A%dB%d exceeds
measurement by %f percent and mean square error of %f percent.\n ',j-1,N-j+1,N-
j+1,j-1,pop_error(1,j)*100,pop_error(2,j)*100);
          end
```

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). GMP2 is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table A.2.4. 4a with TMEDA at –78 °C.





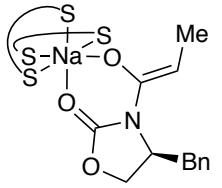


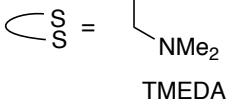
G = –1636.832111
G_{MP2} = –1636.168318

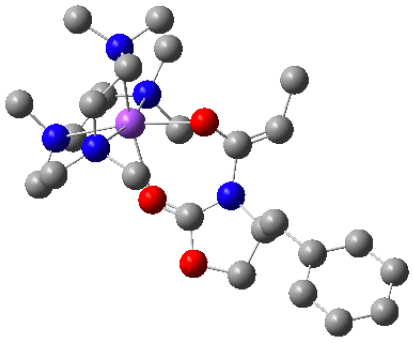
Na	0.00000000	0.00000000	0.00000000	O	1.78018700	-1.17246100	-0.75407000
C	2.76311500	-1.64992600	-0.08949200	N	3.44164200	-0.70334500	0.84316900
C	2.81971900	0.30784100	1.50056700	O	3.74600300	1.10964100	2.12062900
C	5.03144600	0.46944800	2.04322600	H	5.79154200	1.23418200	1.87085500
H	5.23104600	-0.02665800	3.00028200	C	4.89799500	-0.53923500	0.88875000
H	5.38191500	-1.48382500	1.14895200	C	5.46425500	-0.04505900	-0.46345300
H	5.10102700	-0.74008500	-1.22897200	H	5.03745400	0.94094500	-0.68428000
C	6.97499600	0.01707300	-0.48027100	C	7.65619000	1.23887300	-0.39625800
C	9.05205000	1.28495700	-0.38281900	C	9.79175800	0.10424300	-0.45216600
C	9.12626600	-1.12109100	-0.53960500	C	7.73256800	-1.16218700	-0.55450000
H	7.22065300	-2.11897800	-0.63496600	H	9.69417900	-2.04585600	-0.60238200
H	10.8779750	0.13742900	-0.44354300	H	9.55975000	2.24423200	-0.32166600
H	7.08651300	2.16500100	-0.35254600	O	1.62489100	0.56753600	1.59914000
C	3.31946000	-2.89598100	-0.13358200	H	4.11429400	-3.15053000	0.56173300
C	2.86012600	-3.95380100	-1.09695500	H	3.70766000	-4.49470200	-1.54290000
H	2.21671300	-4.72087000	-0.63368400	H	2.28739700	-3.50370200	-1.91549900
N	0.51543500	2.04241100	-1.62128200	C	0.33882700	1.77644800	-3.04805600
H	0.69055300	2.61117200	-3.68451900	H	0.90273800	0.87885600	-3.31860500

H	-0.71957300	1.60239000	-3.26950500	C	1.94395500	2.20953500	-1.33209100
H	2.09316400	2.43098800	-0.27375400	H	2.45515300	1.26748900	-1.54653900
H	2.39256600	3.02462000	-1.93184600	C	-0.27551500	3.20175500	-1.19488200
C	-0.49334400	3.27601900	0.31991700	H	0.47511100	3.26742900	0.82857600
H	-0.96405400	4.25223500	0.55121700	N	-1.28621400	2.17047200	0.88010500
C	-2.69448100	2.25820500	0.49403900	H	-2.80308100	2.19068000	-0.59163800
H	-3.24418500	1.42093900	0.93605800	H	-3.16879300	3.19934300	0.83323100
C	-1.16387700	2.16986300	2.34266400	H	-1.76410900	1.35401000	2.75711300
H	-0.11993500	2.00285000	2.61755300	H	-1.51600400	3.11663500	2.79433100
H	-1.24420500	3.15315900	-1.70449300	H	0.19379100	4.15145500	-1.51877400
N	-0.96813600	-1.96436900	1.43949300	C	-2.10952500	-1.69904700	2.31457900
H	-2.48704600	-2.61676300	2.80609100	H	-1.80591700	-0.99715500	3.09701200
H	-2.93555700	-1.24470200	1.75991200	C	0.16356100	-2.44058600	2.24619800
H	0.45016100	-1.66408000	2.96131500	H	-0.08719700	-3.36250000	2.80492500
H	1.02223500	-2.64273300	1.60141200	C	-1.28645500	-2.94954400	0.39521900
H	-0.34567500	-3.21334900	-0.09698900	H	-1.68818000	-3.88055500	0.84325300
C	-2.29597100	-2.46470900	-0.64876600	H	-3.20263800	-2.11019000	-0.14721800
H	-2.60331900	-3.33985900	-1.25419200	N	-1.81134000	-1.38233600	-1.51911400
C	-2.94327300	-0.74380300	-2.19268200	H	-2.58249700	0.07476100	-2.82359300
H	-3.51036300	-1.44354200	-2.83584800	H	-3.63291300	-0.32602200	-1.45143500
C	-0.85346300	-1.89008800	-2.51329400	H	-0.60587200	-1.08707000	-3.21320800
H	0.07791100	-2.19035000	-2.02858200	H	-1.27188500	-2.73536700	-3.09208500

Table A.2.5. 4b with TMEDA at –78 °C.







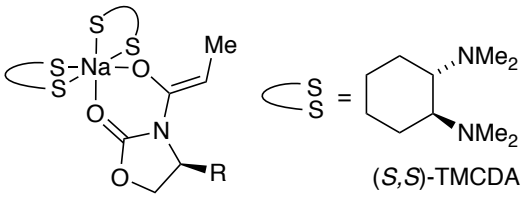
G = –1636.83276

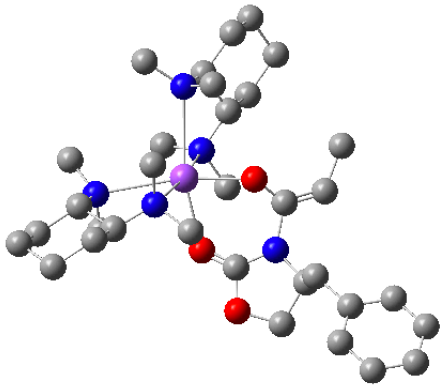
G_{MP2} = –1636.168975

Na	0.00000000	0.00000000	0.00000000	O	1.86394300	-0.43183800	-1.21911200

C	2.77458100	-1.26434700	-0.87641800	N	3.41348800	-1.01648700	0.44810700
C	2.76317700	-0.52109300	1.53106700	O	3.66180900	-0.20332100	2.51838400
C	4.95530900	-0.70792400	2.14159700	H	5.71327800	0.02142200	2.43465800
H	5.13244500	-1.64623800	2.67999600	C	4.86583900	-0.92479400	0.62012700
H	5.34320200	-1.86709300	0.33920000	C	5.47770200	0.21568000	-0.22751900
H	5.14027500	0.05920800	-1.25824100	H	5.06054400	1.17116500	0.11335700
C	6.98844500	0.24591900	-0.16814000	C	7.67035200	1.20388500	0.59414700
C	9.06519200	1.20626100	0.66627200	C	9.80316800	0.24578100	-0.02574200
C	9.13714600	-0.71312600	-0.79312100	C	7.74450700	-0.71086500	-0.86320400
H	7.23288400	-1.45310900	-1.47261200	H	9.70398200	-1.46029900	-1.34276000
H	10.8886510	0.24662300	0.02690900	H	9.57355500	1.96175900	1.25995000
H	7.10272100	1.96421800	1.12680200	O	1.56262300	-0.34783700	1.71440700
C	3.28742700	-2.32879900	-1.55907000	H	4.02295400	-2.96459700	-1.07384700
C	2.86612200	-2.67825200	-2.95838100	H	3.72816300	-2.92300500	-3.59627100
H	2.19167600	-3.54980000	-3.00662500	H	2.33960100	-1.83688500	-3.42155600
N	-0.93335900	-2.50568400	0.09357300	C	0.18844100	-3.22216300	0.71491500
H	0.49090800	-2.72897300	1.64044800	H	-0.07220800	-4.27539900	0.93550000
H	1.04845800	-3.20260800	0.03934100	C	-1.23562000	-3.11160800	-1.20428400
H	-2.06594700	-2.57957600	-1.68087600	H	-0.35762900	-3.03384100	-1.85128400
H	-1.51601000	-4.17912800	-1.12051700	C	-2.12121200	-2.50070500	0.95370000
H	-2.97768000	-2.19639600	0.34121400	H	-2.35285700	-3.51970400	1.32285900
C	-2.00420200	-1.57649400	2.16925800	H	-1.11221500	-1.84254900	2.74390200
H	-2.87153500	-1.76564500	2.83182700	N	-1.90364600	-0.14542500	1.84056200
C	-3.18753600	0.39944700	1.39808500	H	-3.06678400	1.45856400	1.14928500
H	-3.53629900	-0.11592100	0.49893800	H	-3.97345500	0.31328900	2.17297200
C	-1.41537300	0.59853200	3.00758300	H	-0.40517300	0.26324200	3.25543500
H	-1.37171300	1.66435200	2.76650500	H	-2.07085900	0.47284900	3.88996900
N	0.46537900	2.72576300	0.03322400	C	-0.03199400	3.20545600	-1.26353100
H	0.55146500	4.08349200	-1.60429700	H	-1.05720200	3.56255300	-1.11775200
C	-0.00214000	2.16204600	-2.38350700	N	-0.95760900	1.05179900	-2.22324100
C	-2.34461600	1.49250100	-2.36818700	H	-2.60884800	2.21576200	-1.59196200
H	-2.54116900	1.95626400	-3.35415300	H	-3.01140900	0.63070900	-2.25964300
C	-0.65434700	0.01622000	-3.22074700	H	0.34684000	-0.37640000	-3.02656800
H	-1.37653400	-0.80091100	-3.12907300	H	-0.71019900	0.40664000	-4.25466000
H	0.99437800	1.71584600	-2.44559900	H	-0.18411300	2.68968400	-3.34109100
C	1.93095200	2.61912200	0.03938900	H	2.25896700	2.32706500	1.04079100
H	2.25551900	1.83772300	-0.65171400	H	2.41257100	3.58102600	-0.22320800
C	0.03229200	3.62375100	1.10388100	H	-1.06203100	3.66969600	1.13669500
H	0.39077800	3.24428100	2.06542200	H	0.41416600	4.65529800	0.97862800

Table A.2.6. 4a with (*S*,*S*)-TMCDA at –78 °C.



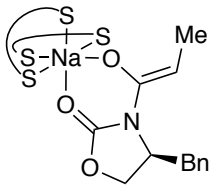


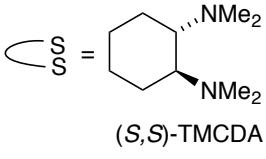
G = –1947.826475
G_{MP2} = –1946.976178

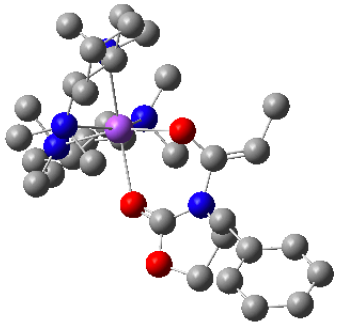
Na	0.00000000	0.00000000	0.00000000	O	1.69134300	-1.24928600	-0.82692500
C	2.63232600	-1.81976700	-0.17394100	N	3.39020200	-0.95054100	0.77066000
C	2.85688600	0.10072600	1.44373000	O	3.85105100	0.82265500	2.05764400
C	5.08117700	0.08379800	1.96057600	H	5.89743600	0.78635200	1.78063900
H	5.25340900	-0.43113400	2.91290000	C	4.85520300	-0.90496600	0.80304400
H	5.26329300	-1.88678000	1.05600500	C	5.44942900	-0.45127100	-0.55135300
H	5.01256500	-1.09815800	-1.32035700	H	5.11701200	0.57378300	-0.75538800
C	6.95877400	-0.53586400	-0.58817600	C	7.75783000	0.61157100	-0.49563300
C	9.15155200	0.52064000	-0.50362500	C	9.77071800	-0.72540600	-0.60370000
C	8.98694000	-1.87797600	-0.69991900	C	7.59590100	-1.78223500	-0.69301400
H	6.99152600	-2.68284300	-0.78037200	H	9.46040100	-2.85264700	-0.78676900
H	10.8549570	-0.79896300	-0.61215600	H	9.75172200	1.42444800	-0.43565000
H	7.28283400	1.58825800	-0.42871200	O	1.68766100	0.45005600	1.56224100
C	3.08301200	-3.10695900	-0.24340600	H	3.85881700	-3.43709300	0.44158400
C	2.54845700	-4.10349400	-1.23237700	H	3.35661000	-4.66485400	-1.72462900
H	1.88435400	-4.85949000	-0.77953600	H	1.97474300	-3.59506300	-2.01489300
N	0.75456100	2.25085900	-1.27134700	C	0.36833500	3.49673000	-0.56889100
C	-1.11268400	3.49267600	-0.10456500	N	-1.47632600	2.27078100	0.65880000
C	-2.92014000	2.03517200	0.65127600	H	-3.28742900	2.00652400	-0.37959500
H	-3.12971300	1.06461200	1.11159500	H	-3.50031900	2.79709300	1.20361900
C	-0.96488500	2.24451400	2.03501300	H	-1.16390400	1.25880800	2.46720500
H	0.11780800	2.38080500	2.04522900	H	-1.43574500	2.99443700	2.69329200
C	-1.44194700	4.81000600	0.64342600	C	-1.13526200	6.06360500	-0.18405300
C	0.33582200	6.06970600	-0.60921300	C	0.67155000	4.78528000	-1.37585300
H	1.72732300	4.78648800	-1.67113400	H	0.08749500	4.77781800	-2.30623600

H	0.55804100	6.94668800	-1.23043600	H	0.97360500	6.14808100	0.28344100
H	-1.37753000	6.96296700	0.39627400	H	-1.77478200	6.08686700	-1.07897100
H	-2.49613600	4.80587500	0.94598300	H	-0.85191400	4.85640600	1.56804600
H	-1.73947900	3.46693800	-1.00668000	H	0.99257100	3.51858800	0.33392900
C	2.20988300	2.07200800	-1.33648300	H	2.64258400	2.25790000	-0.34982600
H	2.42091300	1.03331800	-1.60810000	H	2.69946100	2.74335600	-2.06533600
C	0.17977900	2.09298400	-2.60713300	H	0.46484200	1.10908200	-2.99130700
H	-0.91343700	2.14044300	-2.56796100	H	0.53234100	2.84282600	-3.33720700
N	-1.98919800	-1.49488500	-1.40745700	C	-2.28183900	-2.77978700	-0.71658500
C	-1.24829200	-3.12861600	0.38862100	N	-1.04970500	-2.02021200	1.36323600
C	-2.24174700	-1.64964200	2.12498200	H	-2.62250400	-2.45222300	2.78126400
H	-1.99529300	-0.79896500	2.76941100	H	-3.05017600	-1.33951200	1.45731100
C	0.06091700	-2.29737000	2.28597900	H	0.34361000	-1.37154300	2.79576200
H	-0.19117100	-3.05058200	3.05297000	H	0.92978900	-2.64753000	1.72160000
H	-0.27089600	-3.25188100	-0.09412400	C	-1.62955100	-4.47169200	1.06575200
H	-2.56669200	-4.34428200	1.62572900	H	-0.86165300	-4.73693700	1.80015000
C	-1.81422000	-5.62753100	0.07575600	C	-2.86653700	-5.26715100	-0.97566700
C	-2.46476100	-3.97194700	-1.68855000	H	-3.21132100	-3.70741400	-2.44827000
H	-1.52395200	-4.15402600	-2.22274900	H	-2.98236000	-6.07703100	-1.70726500
H	-3.84533700	-5.14098300	-0.48888400	H	-2.09742700	-6.53991100	0.61620400
H	-0.85870300	-5.84229800	-0.42433200	H	-3.24993700	-2.63187600	-0.22027600
C	-3.21121600	-0.84822900	-1.88304100	H	-2.96055700	0.13204900	-2.30400500
H	-3.74241500	-1.41851100	-2.66831500	H	-3.90388000	-0.69008300	-1.04962200
C	-1.01859700	-1.60559200	-2.50531000	H	-0.81937800	-0.60055600	-2.88923600
H	-0.06974600	-2.00534300	-2.13971500	H	-1.38159200	-2.20983600	-3.35417700

Table A.2.7. 4b with (*S*,*S*)-TMCDA at –78 °C.







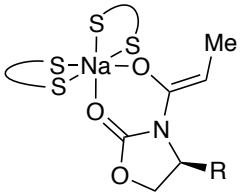
G = –1947.825997

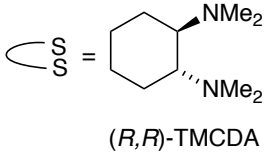
$G_{MP2} = -1946.976005$

Na	0.00000000	0.00000000	0.00000000	O	-1.90030700	-0.14397300	1.18271400
C	-2.58834600	-1.20126500	1.41318700	N	-3.01793100	-1.96578000	0.20998000
C	-4.40579600	-2.37198600	-0.02414100	C	-4.24935400	-3.15839600	-1.33842400
O	-3.01924000	-2.67919900	-1.91058600	C	-2.27970800	-2.08199900	-0.92189500
O	-1.11972100	-1.74564200	-1.13801500	H	-5.05692700	-2.98187900	-2.05182100
H	-4.15432200	-4.23626800	-1.16277400	H	-4.75194000	-3.03041400	0.77688600
C	-5.35288700	-1.15203600	-0.11357200	H	-5.19284100	-0.56241400	0.79622600
H	-5.04715600	-0.53178000	-0.96517000	C	-6.80810200	-1.54341300	-0.23891100
C	-7.48577000	-1.45172900	-1.46214500	C	-8.82190000	-1.84248500	-1.57531800
C	-9.50390200	-2.33400900	-0.46203200	C	-8.84224700	-2.42770700	0.76487900
C	-7.50863700	-2.03514200	0.87351300	H	-7.00302900	-2.09926900	1.83489100
H	-9.36786300	-2.80157500	1.63986000	H	-10.5441280	-2.63690400	-0.54708600
H	-9.32941100	-1.75852800	-2.53295400	H	-6.96426700	-1.05851900	-2.33245200
C	-3.02323000	-1.71626600	2.59828300	H	-3.54486100	-2.66953800	2.60229900
C	-2.79105600	-1.03384200	3.91623500	H	-3.70136200	-1.01382100	4.53383300
H	-2.01519000	-1.52286600	4.52829400	H	-2.47409100	0.00264400	3.75887900
N	0.11459000	2.51434600	0.93913700	C	-1.19908900	3.14878400	0.63437300
C	-1.38010400	3.47072600	-0.87479000	N	-1.09259000	2.31758200	-1.76232500
C	-2.19235400	1.35287000	-1.87825400	H	-1.83100800	0.46899300	-2.41293200
H	-2.51301200	1.02565100	-0.88503900	H	-3.06347300	1.74706000	-2.43184800
C	-0.65714600	2.74776400	-3.08854400	H	0.22519000	3.39254900	-3.00660200
H	-0.38114100	1.86939200	-3.68215300	H	-1.43034100	3.29692200	-3.65897100
H	-0.63260800	4.23239800	-1.13564200	C	-2.76892100	4.10909100	-1.12589600
C	-3.00177100	5.37366700	-0.29262800	C	-2.84332600	5.05383000	1.19577200
C	-1.47011800	4.42829900	1.47055200	H	-1.38444900	4.19472400	2.53707100
H	-0.69668000	5.17825200	1.25177600	H	-2.97032600	5.95783000	1.80519800
H	-3.63457400	4.35473300	1.50328800	H	-3.99879600	5.78310500	-0.49997900
H	-2.27736200	6.15016800	-0.58080000	H	-2.87699400	4.33249900	-2.19469200
H	-3.55252100	3.38203200	-0.87690700	H	-1.94115400	2.39061800	0.91420400
C	1.28188500	3.33870600	0.62721200	H	1.28907100	3.61445300	-0.43062900
H	1.35153700	4.26240500	1.22838100	H	2.18747300	2.75428100	0.82280900
C	0.18124800	2.04816200	2.32940400	H	-0.66348300	1.38105500	2.52188800
H	1.10769000	1.48025100	2.46503100	H	0.18902100	2.86350300	3.07369000
N	2.07130400	-0.58658800	-1.41576600	C	2.75153400	-1.82851400	-0.96227100
C	2.95079400	-1.88434300	0.57737500	N	1.69641700	-1.63174900	1.33035700
C	0.75448800	-2.76201500	1.34423400	H	0.52977500	-3.08233700	0.32488000
H	1.12715700	-3.62566800	1.92114900	H	-0.18573400	-2.43478700	1.79792300
C	1.95973500	-1.20297500	2.70556900	H	2.63580100	-0.34069100	2.70773500

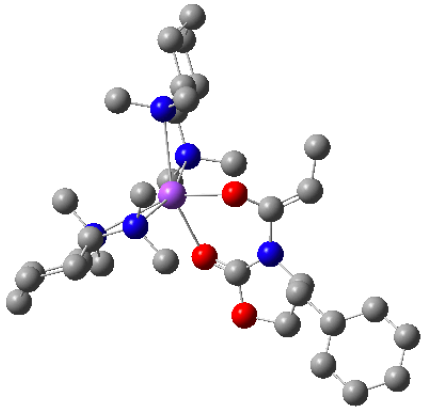
H	1.01644300	-0.90308500	3.17209900	H	2.40933400	-1.99083200	3.33658200
H	3.62408900	-1.05908200	0.84925200	C	3.66253300	-3.20299500	0.97743400
H	3.82342700	-3.21519500	2.06214300	H	3.00387500	-4.05144300	0.75114300
C	4.99176100	-3.41839400	0.24496600	H	5.44239700	-4.36804300	0.56013300
H	5.70448100	-2.62699500	0.52100900	C	4.76912700	-3.39786300	-1.26959600
C	4.09643600	-2.08502800	-1.68747500	H	4.78900200	-1.26089400	-1.46841400
H	3.93344700	-2.07422600	-2.77145400	H	5.71896200	-3.51889200	-1.80578800
H	4.13568400	-4.24979500	-1.55697300	H	2.06668100	-2.64199800	-1.23397700
C	2.90442100	0.61807100	-1.37473300	H	2.26772100	1.49084800	-1.55068400
H	3.36412300	0.73282300	-0.38861800	H	3.70676200	0.62997000	-2.13272600
C	1.47852400	-0.74569800	-2.74870500	H	0.77417400	-1.58022600	-2.73960000
H	0.91735200	0.16131000	-2.99476900	H	2.22559300	-0.90129600	-3.54732200

Table A.2.8. 4a with (*R*,*R*)-TMCDA at –78 °C.





(*R*,*R*)-TMCDA



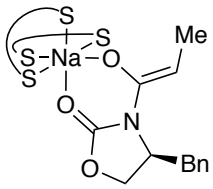
G = –1947.826729

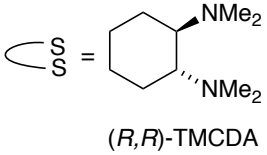
G_{MP2} = –1946.976863

Na	0.00000000	0.00000000	0.00000000	O	1.63823800	-1.16363400	-1.01249900
C	2.53732400	-1.91123100	-0.49312000	N	3.29417400	-1.32011700	0.65124800
C	2.78315700	-0.42287400	1.53241100	O	3.77878200	0.07287100	2.33614900
C	4.97418200	-0.69516600	2.11367300	H	5.83150100	-0.01921800	2.13074300
H	5.07524900	-1.42351200	2.92677100	C	4.75588600	-1.37778400	0.75140800
H	5.09532900	-2.41599600	0.78739900	C	5.44456400	-0.66853600	-0.43852400
H	5.02374700	-1.10613100	-1.35076500	H	5.16788600	0.39291800	-0.42385700
C	6.94855600	-0.82334700	-0.42283200	C	7.78737700	0.23059100	-0.03617600
C	9.17412200	0.06898800	0.00445300	C	9.74618900	-1.15533800	-0.34175500
C	8.92267500	-2.21405000	-0.73271500	C	7.53883600	-2.04773500	-0.77316300

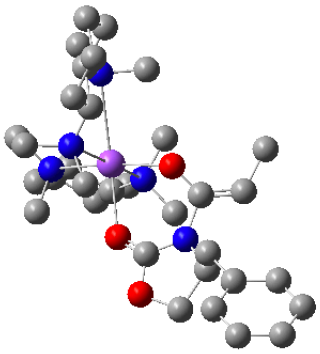
H	6.90413900	-2.87266900	-1.09023600	H	9.35983400	-3.16924000	-1.01239100
H	10.8250000	-1.28339300	-0.31273200	H	9.80599500	0.90163300	0.30304200
H	7.34964700	1.19212400	0.22451800	O	1.62669500	-0.04227200	1.68883800
C	2.94377800	-3.16108500	-0.85813500	H	3.67863300	-3.68378900	-0.25268800
C	2.38123500	-3.87236800	-2.05620200	H	3.16379400	-4.39471400	-2.62577500
H	1.62658700	-4.63548300	-1.80017600	H	1.89989200	-3.15719400	-2.73241700
N	-1.40089900	-1.83101700	1.35480800	C	-1.64701400	-1.35958000	2.71851300
H	-1.91953300	-2.16332800	3.42640200	H	-0.73784100	-0.88008500	3.09408100
H	-2.45752200	-0.62152200	2.71986700	C	-0.29557900	-2.80112000	1.36365700
H	0.58860700	-2.30569800	1.76816200	H	-0.50274000	-3.69192200	1.98081900
H	-0.04576600	-3.11815300	0.34971500	C	-2.63888700	-2.30967800	0.69113400
H	-3.39173100	-1.53002600	0.88078300	C	-2.47379400	-2.43300200	-0.84711600
N	-1.96612100	-1.18538300	-1.47712400	C	-2.99065400	-0.16679000	-1.71274100
H	-2.49905000	0.77193700	-1.99098500	H	-3.69921800	-0.42215200	-2.51968400
H	-3.56499600	0.01683900	-0.79978000	C	-1.23326800	-1.47761800	-2.71526100
H	-0.91149800	-0.53736100	-3.17058000	H	-0.33319200	-2.04955700	-2.47860700
H	-1.83890800	-2.01960900	-3.46399300	H	-1.69483800	-3.18337600	-1.02916500
C	-3.77783200	-2.95990500	-1.49753200	H	-4.57503000	-2.21466100	-1.37265600
H	-3.62434300	-3.07267700	-2.57762500	C	-4.26380800	-4.28080200	-0.89055400
C	-4.47542800	-4.11845900	0.61695200	C	-3.18267800	-3.63492000	1.28434600
H	-2.42299200	-4.41861800	1.16775200	H	-3.33950900	-3.51326300	2.36253200
H	-5.28421300	-3.39412100	0.79579500	H	-4.79819600	-5.06440400	1.07007200
H	-5.19130500	-4.59952200	-1.38309000	H	-3.52301900	-5.07278400	-1.07368600
N	-0.85405300	2.45981000	1.08413000	C	-0.15024100	3.62382200	0.48687700
C	0.10543600	3.46051400	-1.03607900	N	0.76540500	2.17554200	-1.36109200
C	0.65327500	1.82442600	-2.77764700	H	1.23241700	2.48641600	-3.44716200
H	1.02301800	0.80339700	-2.91165400	H	-0.39654600	1.86431300	-3.09097900
C	2.17320400	2.08090200	-0.94989300	H	2.27895800	2.32081700	0.11093600
H	2.48813500	1.04393400	-1.09388100	H	2.83961200	2.74218700	-1.53101800
H	-0.87538800	3.41956000	-1.53311000	C	0.85108300	4.70198300	-1.59081600
C	0.13884000	6.02465400	-1.28483000	C	-0.06571100	6.18031100	0.22463500
C	-0.84113900	4.97992400	0.77925700	H	-1.84351700	4.98150400	0.33012500
H	-0.98487900	5.08975500	1.86102900	H	-0.60207300	7.11037200	0.45214400
H	0.91332300	6.25359700	0.72057200	H	-0.83836600	6.04893300	-1.78971400
H	0.71899500	6.86440300	-1.68809900	H	1.85703100	4.74204400	-1.15281500
H	0.98850900	4.58999900	-2.67284700	H	0.83019000	3.64774900	0.97876000
C	-2.29841600	2.44130300	0.85117900	H	-2.51649000	2.58402300	-0.21109600
H	-2.69234200	1.46153800	1.14318700	H	-2.85372000	3.20653200	1.42173700
C	-0.56483600	2.33314400	2.51548300	H	-1.07938200	1.45220300	2.90854300
H	0.50681300	2.17962000	2.66272500	H	-0.89635500	3.20443800	3.10949000

Table A.2.9. 4b with (*R*,*R*)-TMCDA at –78 °C.





(*R*,*R*)-TMCDA

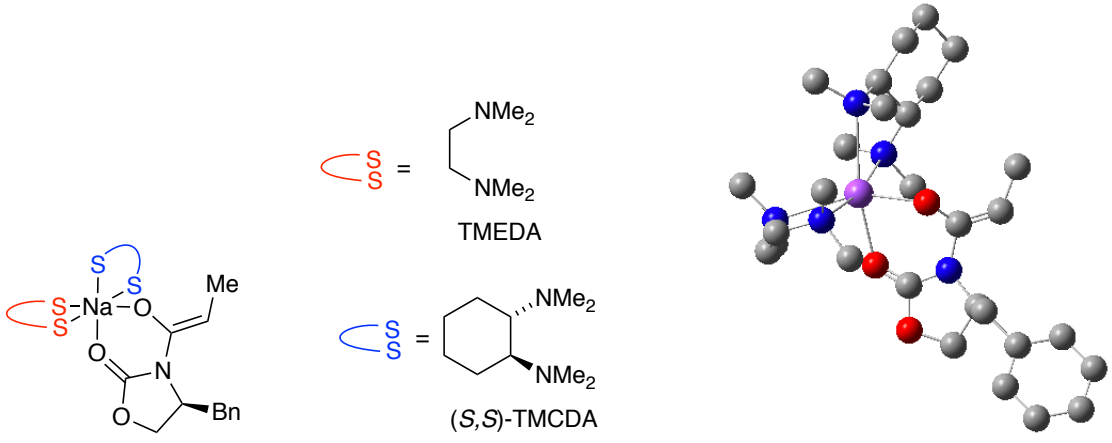


G = –1947.82383
G_{MP2} = –1946.975166

Na	0.00000000	0.00000000	0.00000000	O	-1.86724800	0.10961300	1.23277800
C	-2.70513400	-0.82533400	1.48007200	N	-3.24279900	-1.54364500	0.28909400
C	-2.56148300	-1.73640200	-0.87103200	O	-3.38850900	-2.29055400	-1.81652300
C	-4.61880700	-2.67863200	-1.18329200	H	-5.44561600	-2.45804200	-1.86162700
H	-4.58836600	-3.75824900	-0.99470200	C	-4.66274300	-1.86645700	0.12346000
H	-5.01184500	-2.49343200	0.94774200	C	-5.53955500	-0.59383900	0.05713400
H	-5.29704200	0.00271400	0.94375400	H	-5.24545300	-0.01012200	-0.82394200
C	-7.01942900	-0.90218800	0.01766600	C	-7.75596700	-0.79755100	-1.16989500
C	-9.11589100	-1.11428100	-1.20340400	C	-9.76303200	-1.54350300	-0.04447900
C	-9.04236000	-1.64911100	1.14773000	C	-7.68516000	-1.33047500	1.17682100
H	-7.13249700	-1.40356500	2.11127600	H	-9.53989500	-1.97481500	2.05771800
H	-10.8214590	-1.78903400	-0.06733100	H	-9.66879100	-1.02162700	-2.13473800
H	-7.26090800	-0.45293400	-2.07553800	O	-1.39059300	-1.50166000	-1.14886000
C	-3.20612500	-1.24712300	2.67809300	H	-3.87097300	-2.10546000	2.70949900
C	-2.85499900	-0.58509800	3.98013700	H	-3.74821900	-0.30208400	4.55835100
H	-2.25330600	-1.22973600	4.64154400	H	-2.27613100	0.32591100	3.79729700
N	2.33084900	-0.78572600	-1.13625500	C	3.13428000	0.37342600	-1.52866500
H	2.48228700	1.13203400	-1.97158300	H	3.61081500	0.80997800	-0.64577600
H	3.92238200	0.14016100	-2.26690400	C	1.68045900	-1.37021400	-2.31600200
H	1.02513600	-2.19326900	-2.02710200	H	1.04474300	-0.61004300	-2.78179200
H	2.39269900	-1.72147700	-3.08207500	C	3.11822700	-1.74914300	-0.32282300
H	3.61295800	-1.13568900	0.44408600	C	2.23293500	-2.79120800	0.41171900
N	1.11008900	-2.18100500	1.16041600	C	0.00566100	-3.12803600	1.35080900
H	-0.33968800	-3.48313300	0.37629100	H	0.28334000	-3.99992400	1.97145300
H	-0.83040500	-2.61914100	1.83895700	C	1.47997100	-1.58182300	2.44413800

H	2.30769600	-0.87602800	2.31416200	H	0.61566600	-1.03204900	2.82935800
H	1.77620600	-2.31858800	3.21137300	H	1.75963200	-3.41287300	-0.35943300
C	3.11762800	-3.72939400	1.27110900	H	3.60215000	-3.14554200	2.06541200
H	2.48038200	-4.46760700	1.77211300	C	4.20679800	-4.43619200	0.45659900
H	4.81025300	-5.07788400	1.11115700	H	3.74242200	-5.09763200	-0.28947400
C	5.08767200	-3.40532400	-0.25472900	H	5.63492400	-2.81451100	0.49492000
H	5.84558800	-3.90084100	-0.87466100	C	4.23116000	-2.47529300	-1.12301400
H	3.76978000	-3.07312500	-1.92041400	H	4.87110700	-1.73647500	-1.61938000
N	-0.83321800	2.20803900	-1.27409300	C	-2.10536500	1.63743000	-1.73400300
H	-1.89996400	0.75161600	-2.34218400	H	-2.68139900	1.31891900	-0.86212700
H	-2.70553100	2.33659600	-2.34272200	C	-0.01063500	2.58190600	-2.42422600
H	0.95158300	2.98707900	-2.09855500	H	0.18783900	1.68479400	-3.02161800
H	-0.48547800	3.31963700	-3.09498800	C	-1.04824800	3.29116000	-0.27683600
C	0.25049400	3.69194700	0.47548000	N	0.95180600	2.53732700	1.09506700
C	2.38366300	2.79182100	1.24102200	H	2.81912500	3.06021800	0.27279500
H	2.62517900	3.59627600	1.96089200	H	2.87910300	1.88002000	1.59392800
C	0.38625700	2.10094700	2.37903400	H	-0.66254100	1.81842200	2.26327900
H	0.92457500	1.20610700	2.70463300	H	0.48827900	2.85087500	3.18223900
H	0.94902500	4.08923400	-0.27307300	C	-0.03305900	4.84120000	1.47679300
H	0.90039100	5.11926500	1.98194700	H	-0.71497300	4.48084500	2.25726400
C	-0.66885800	6.07020100	0.82039500	H	-0.84667600	6.84818700	1.57383400
H	0.02117400	6.50144100	0.07977900	C	-1.97434600	5.66921300	0.13017300
H	-2.69510000	5.32456500	0.88582800	H	-2.43363900	6.53130600	-0.37039700
C	-1.71546000	4.55267700	-0.88793600	H	-1.06866600	4.95528900	-1.67986400
H	-2.65696500	4.26912800	-1.37113500	H	-1.73766700	2.85795800	0.45857900

Table A.2.10. 4a with TMEDA and (*S*,*S*)-TMCDA at –78 °C.

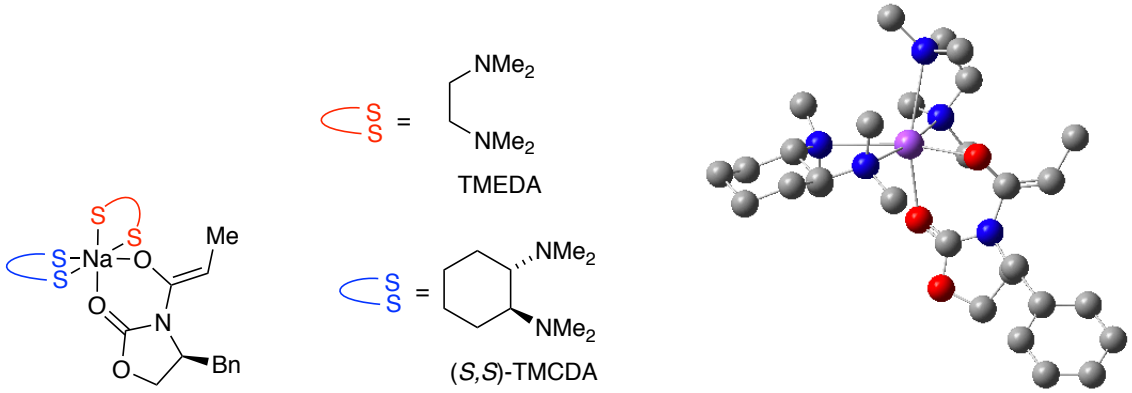


G = –1792.329366
G_{MP2} = –1791.572685

Na	0.00000000	0.00000000	0.00000000	O	-1.55419200	-1.42334400	0.81177000
C	-2.42062400	-2.08710800	0.14783700	N	-3.28563600	-1.29184800	-0.77202400
C	-2.90174500	-0.14856600	-1.39342300	O	-3.97836000	0.44346600	-2.00504600
C	-5.08888200	-0.46960100	-1.96215300	H	-6.00218900	0.10021500	-1.77963700
H	-5.16527000	-0.96966200	-2.93476600	C	-4.74162800	-1.45510100	-0.83286700
H	-4.99981400	-2.47588300	-1.12539700	C	-5.41459000	-1.13698700	0.52343000
H	-4.90114700	-1.74151700	1.27936100	H	-5.23539200	-0.08246900	0.76692300
C	-6.89679300	-1.43666200	0.52612700	C	-7.85026200	-0.41286900	0.44568400
C	-9.21636200	-0.70265900	0.41683700	C	-9.65183200	-2.02697400	0.46722800
C	-8.71270000	-3.05794100	0.55143100	C	-7.35001800	-2.76391600	0.58141800
H	-6.62415100	-3.57082900	0.65875300	H	-9.04281300	-4.09253300	0.59970200
H	-10.7141860	-2.25509300	0.44665100	H	-9.93875800	0.10757500	0.35890400
H	-7.51903000	0.62326400	0.41745700	O	-1.79378200	0.37411900	-1.47277300
C	-2.70503200	-3.42261800	0.18422500	H	-3.43526800	-3.83549200	-0.50556700
C	-2.02225700	-4.36262200	1.13726300	H	-2.72656800	-5.08847800	1.56901100
H	-1.21765200	-4.95657200	0.67015700	H	-1.57081400	-3.80443400	1.96509100
N	1.22636900	-1.78365400	-1.46717200	C	2.26793200	-1.15948300	-2.28193800
H	2.76176500	-1.85154200	-2.98693900	H	1.80978700	-0.36411200	-2.87797100
H	3.03642700	-0.70293700	-1.65137400	C	0.12605000	-2.24064200	-2.32675600
H	-0.34912800	-1.36962400	-2.78832000	H	0.45625800	-2.92027000	-3.13212300
H	-0.62821500	-2.75182400	-1.72160500	C	1.70005700	-2.85288000	-0.54963200
H	0.79795800	-3.18946800	-0.02278300	C	2.69951600	-2.32789100	0.51449100
H	3.59005200	-1.97489700	-0.02204600	N	2.18652400	-1.14368500	1.25439100
C	3.27180000	-0.29016300	1.73479100	H	2.84751300	0.61438000	2.18513400
H	3.91325200	-0.76968100	2.49753200	H	3.90861700	0.01689400	0.89811500
C	1.27022100	-1.46891300	2.35631700	H	0.87207800	-0.53401800	2.76010800
H	0.41654300	-2.04354500	1.98982800	H	1.75614100	-2.00634000	3.18836600
C	3.16672800	-3.47857600	1.44010600	H	3.88764000	-3.08731900	2.16917700
H	2.31069500	-3.85273000	2.01557400	C	3.77562500	-4.65425600	0.66738700
H	4.08578500	-5.44134500	1.36648800	H	4.68404200	-4.32682800	0.13974800
C	2.76249600	-5.19272100	-0.34515400	H	1.89434400	-5.60222500	0.19151200
H	3.19145300	-6.02021600	-0.92464500	C	2.30424400	-4.07548600	-1.29014300
H	1.56699200	-4.46998400	-1.99772300	H	3.16765800	-3.75062700	-1.88757700
N	-0.76349500	1.97313100	1.74554500	C	-0.46914000	1.83469400	3.17203100
H	-0.94438000	2.62697500	3.78172200	H	-0.83719900	0.86769100	3.52729900
H	0.61240800	1.87869500	3.34061600	C	-2.21034700	1.82781100	1.53810400

H	-2.45840600	1.97541800	0.48586900	H	-2.50309800	0.80822700	1.80130200
H	-2.78564200	2.55397200	2.14392500	C	-0.26278900	3.25751800	1.24146600
C	-0.16650100	3.34087300	-0.28431500	H	-1.14062900	3.11242700	-0.72600600
H	0.06480100	4.39159000	-0.55104400	N	0.80977600	2.42719100	-0.89973500
C	2.18751300	2.80146400	-0.57681000	H	2.36537000	2.73655400	0.49975000
H	2.87638200	2.10797600	-1.06927400	H	2.43597000	3.82814400	-0.90823500
C	0.61806900	2.43602900	-2.35528600	H	1.36076000	1.78466400	-2.82568400
H	-0.37804500	2.05452100	-2.59083900	H	0.73392900	3.44859800	-2.78618400
H	0.72472700	3.42868700	1.68418100	H	-0.90028100	4.09611500	1.58483900

Table A.2.11. 4a with (*S*,*S*)-TMCDA and TMEDA at –78 °C.



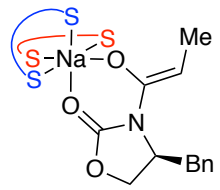
G = –1792.329831

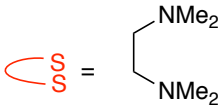
G_{MP2} = –1791.572979

Na	0.00000000	0.00000000	0.00000000	O	1.96176100	-0.74005200	-0.85056800
C	3.03978900	-1.05129200	-0.23320700	N	3.52717000	-0.06038700	0.76626800
C	2.72040400	0.74519900	1.50389900	O	3.47175600	1.68246900	2.17062800
C	4.86106000	1.33737600	2.03591200	H	5.43848900	2.25506600	1.90681400
H	5.18560900	0.83538200	2.95490700	C	4.91776900	0.39987500	0.81642900
H	5.59181000	-0.43803300	1.01185500	C	5.34715400	1.08782000	-0.50095000
H	5.11871000	0.38688500	-1.31176200	H	4.72509300	1.97853100	-0.65090000
C	6.81337700	1.45686100	-0.52061200	C	7.23473500	2.78385100	-0.36155700
C	8.59239100	3.11186700	-0.35437300	C	9.55436500	2.11297400	-0.50547900
C	9.14917000	0.78584900	-0.66818500	C	7.79264600	0.46328000	-0.67637000
H	7.48388900	-0.57073600	-0.81595300	H	9.89116900	0.00158300	-0.79487500
H	10.6113390	2.36568800	-0.50191000	H	8.89646400	4.14860600	-0.23431100
H	6.49050600	3.57045400	-0.25444700	O	1.50238200	0.73106700	1.63661200

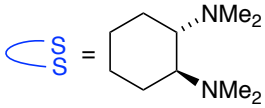
C	3.84107300	-2.14670900	-0.38145600	H	4.68770200	-2.28049100	0.28582300
C	3.59654400	-3.19971200	-1.42508300	H	4.52469800	-3.48632100	-1.94143600
H	3.17295700	-4.13234200	-1.01626000	H	2.89729600	-2.83152400	-2.18350100
N	-0.50198800	-2.26979600	1.25981400	C	-1.68575500	-2.42778900	2.10490900
H	-1.77053200	-3.44945500	2.52342700	H	-1.62931700	-1.72429500	2.94190000
H	-2.60090100	-2.21233900	1.54716700	C	0.70065700	-2.47935800	2.07928600
H	0.75000500	-1.71191300	2.85698200	H	0.69801000	-3.47532600	2.56190600
H	1.59490000	-2.39540700	1.45791600	C	-0.49806600	-3.21384800	0.13010100
H	0.48377200	-3.13985300	-0.34579300	H	-0.60567600	-4.25504800	0.49462800
C	-1.59423800	-2.97321600	-0.91203400	H	-2.56851700	-2.91282800	-0.41595700
H	-1.63953100	-3.86686800	-1.56485900	N	-1.42594200	-1.75619200	-1.72215500
C	-2.68976400	-1.41685400	-2.37758200	H	-2.56685800	-0.49751300	-2.95918900
H	-3.04334000	-2.20917100	-3.06501700	H	-3.46775000	-1.24614700	-1.62614600
C	-0.37196100	-1.93640500	-2.73146500	H	-0.35221300	-1.06126100	-3.38799700
H	0.60678400	-2.00301800	-2.25240100	H	-0.55309500	-2.83011000	-3.35868400
N	-2.02814400	1.66136200	0.76383800	C	-3.32445100	0.98442900	0.76638300
H	-3.66437200	0.82913600	-0.26278000	H	-3.21785300	0.00412900	1.24115500
H	-4.11438900	1.53203000	1.31223200	C	-1.52277600	1.79694400	2.13592700
H	-1.39484800	0.79762200	2.56431400	H	-0.53860400	2.26845100	2.13807200
H	-2.19995900	2.36124600	2.79986100	C	-2.07274200	2.93043400	-0.00727900
C	-0.67054100	3.40532500	-0.47455300	N	0.09727600	2.33990400	-1.15855000
C	1.53684200	2.61845000	-1.19468900	H	1.87942300	2.88966300	-0.19212400
H	2.05910100	1.70557600	-1.49626400	H	1.80618500	3.43346700	-1.89102800
C	-0.37473400	2.00054700	-2.50165400	H	0.17162100	1.11741200	-2.84708900
H	-1.44160000	1.75660400	-2.48602500	H	-0.21382500	2.80158300	-3.24459700
H	-0.08984600	3.64232700	0.42661700	C	-0.79730500	4.71105000	-1.30027700
H	0.20227100	5.04870200	-1.59854300	H	-1.34530600	4.50146000	-2.22902800
C	-1.52983300	5.82904400	-0.54937500	H	-1.60346100	6.72194600	-1.18309800
H	-0.95070100	6.12180900	0.33869400	C	-2.91984800	5.35521200	-0.11473600
C	-2.80657300	4.07967900	0.72898300	H	-3.80360300	3.74121300	1.03608100
H	-2.26248700	4.32360500	1.65102900	H	-3.43679900	6.13662700	0.45663200
H	-3.53519100	5.16003800	-1.00561000	H	-2.65628300	2.69796400	-0.90900800

Table A.2.12. 4b with TMEDA and (*S*,*S*)-TMCDA at –78 °C.

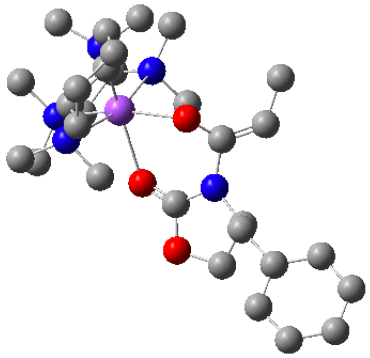




TMEDA



(*S*,*S*)-TMCDA



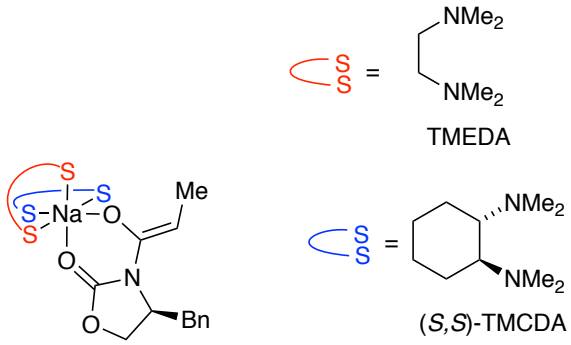
G = –1792.328649

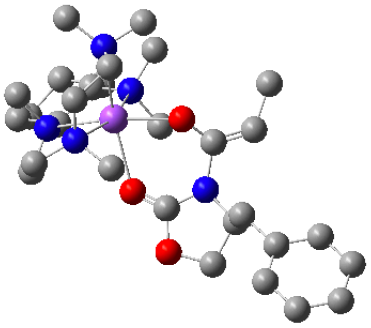
G_{MP2} = –1791.572442

Na	0.00000000	0.00000000	0.00000000	O	-1.81054800	0.53010300	1.24295700
C	-2.80192100	-0.24554500	1.47514900	N	-3.50178300	-0.77932500	0.27040100
C	-2.88527200	-1.09732900	-0.89421600	O	-3.81420200	-1.36439800	-1.86647100
C	-5.11678300	-1.41360300	-1.25637800	H	-5.83453100	-0.94058200	-1.92970000
H	-5.39467400	-2.46460500	-1.11586000	C	-4.95161100	-0.67559200	0.08471200
H	-5.47684600	-1.20766000	0.88216800	C	-5.42614100	0.79655400	0.06945500
H	-5.04148300	1.26137800	0.98428100	H	-4.95856500	1.30816300	-0.78074000
C	-6.93126600	0.92802400	0.00405000	C	-7.58063200	1.30270800	-1.17987100
C	-8.97309800	1.39426100	-1.23874400	C	-9.74131200	1.10990700	-0.10955200
C	-9.10745700	0.73803500	1.07870000	C	-7.71694800	0.64940600	1.13329200
H	-7.22922900	0.37080300	2.06522700	H	-9.69723900	0.52252100	1.96604500
H	-10.8248260	1.18221300	-0.15204700	H	-9.45552700	1.69149100	-2.16641300
H	-6.98811400	1.53714200	-2.06189100	O	-1.68672900	-1.17566500	-1.15160400
C	-3.34992800	-0.63100800	2.66356200	H	-4.16055400	-1.35467700	2.66498200
C	-2.86436500	-0.11013100	3.98664200	H	-3.69813100	0.15776000	4.65219600
H	-2.24840800	-0.83656100	4.54300500	H	-2.25304300	0.78726600	3.84218100
N	-0.14589500	2.47035900	-1.53956000	C	0.17946700	3.60810700	-0.64244100
H	1.18198200	3.94080800	-0.94337600	C	0.26205400	3.20541000	0.85562200
N	1.15429800	2.03614400	1.09186900	C	2.55932900	2.24474700	0.74472400
H	2.65844200	2.54999900	-0.30034100	H	3.07229100	2.99242300	1.37515900
H	3.09441600	1.29581400	0.86348900	C	1.03562800	1.53188000	2.46519600
H	-0.01361800	1.30272000	2.66945100	H	1.61147500	0.60456500	2.55051900
H	1.42223200	2.22758100	3.23034400	H	-0.73117700	2.85991300	1.16875600
C	0.64268400	4.44487500	1.70831500	C	-0.29880500	5.63760000	1.50201100
C	-0.34837700	6.03205100	0.02405400	C	-0.76169100	4.82500900	-0.82449500
H	-0.79610900	5.09989700	-1.88634500	H	-1.78278000	4.53858400	-0.54216800
H	-1.04980100	6.86106100	-0.13542500	H	0.64135300	6.39318200	-0.29351600

H	0.02777200	6.48296200	2.12124800	H	-1.31052200	5.37210700	1.84157200
H	0.65726100	4.17006000	2.76848100	H	1.66427600	4.76230600	1.45469600
C	-1.57844200	2.16163800	-1.64281800	H	-1.69132000	1.23548000	-2.21435100
H	-1.99656600	1.98194300	-0.64867400	H	-2.15953600	2.94817900	-2.15552300
C	0.42522100	2.65215900	-2.87186800	H	1.51266500	2.77078500	-2.80473800
H	0.21596500	1.76423800	-3.47750300	H	0.01899700	3.52484500	-3.41775600
N	0.77784000	-2.29741000	1.31778800	C	-0.48939100	-3.04126000	1.29715400
H	-0.89094200	-3.08088200	0.28374400	H	-0.36047200	-4.07384600	1.67558100
H	-1.22633600	-2.52350500	1.91791100	C	1.25467500	-2.20474200	2.69897800
H	2.19195600	-1.63925400	2.73657100	H	0.50999900	-1.68227200	3.30619000
H	1.43673200	-3.19818100	3.15171800	C	1.79253500	-2.93384000	0.46922600
H	2.76703400	-2.51135500	0.73808700	H	1.86040600	-4.02001300	0.67822300
C	1.55457600	-2.76169100	-1.03360500	H	0.54964700	-3.11072100	-1.28713000
H	2.26421700	-3.42259800	-1.56947500	N	1.67059600	-1.37760300	-1.52249500
C	3.05896100	-0.91339900	-1.51572600	H	3.09918000	0.11699700	-1.88178400
H	3.46595100	-0.92126100	-0.50085200	H	3.71430100	-1.53521800	-2.15540300
C	1.12407200	-1.29218800	-2.88255900	H	0.06012300	-1.53914900	-2.86169900
H	1.23496300	-0.26898800	-3.25347000	H	1.64436200	-1.96936300	-3.58595600

Table A.2.13. 4b with (*S*,*S*)-TMCDA and TMEDA at –78 °C.



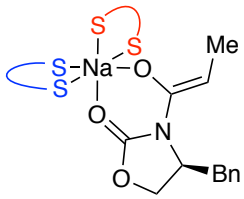


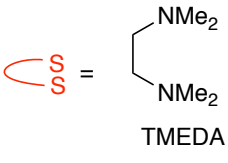
G = –1792.330877
G_{MP2} = –1791.573569

Na	0.00000000	0.00000000	0.00000000	O	-1.88224800	-0.25973800	1.22135900
C	-2.65450300	-1.28294200	1.20379200	N	-3.18242800	-1.67292200	-0.13252900
C	-2.50083700	-1.52576500	-1.29791300	O	-3.32692300	-1.78630900	-2.36321700
C	-4.55654900	-2.34126400	-1.86552300	H	-5.38374200	-1.94238400	-2.45622600
H	-4.52098100	-3.43029300	-1.98654200	C	-4.60332700	-1.92855300	-0.38313100

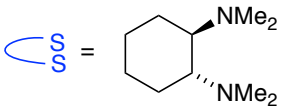
H	-4.95728500	-2.75915800	0.23294000	C	-5.47363600	-0.68342900	-0.09112700
H	-5.22798600	-0.35874100	0.92623300	H	-5.17614900	0.12127900	-0.77459200
C	-6.95515200	-0.96088600	-0.21180400	C	-7.69267600	-0.52334200	-1.32012900
C	-9.05473000	-0.80990600	-1.43664600	C	-9.70315900	-1.54272300	-0.44235200
C	-8.98152100	-1.98240700	0.67021200	C	-7.62221300	-1.69276300	0.78300400
H	-7.06881300	-2.02826000	1.65777500	H	-9.47993500	-2.54675300	1.45429300
H	-10.7632540	-1.76550400	-0.52964700	H	-9.60830900	-0.45644800	-2.30283700
H	-7.19716600	0.05870300	-2.09454000	O	-1.33017500	-1.21805800	-1.49008100
C	-3.10013100	-2.05290800	2.23798400	H	-3.70155600	-2.93243300	2.02539100
C	-2.77353200	-1.75469600	3.67378100	H	-3.65781900	-1.84396200	4.32197800
H	-2.01277300	-2.43160500	4.09717500	H	-2.39014400	-0.73383700	3.77514300
N	-0.87965100	2.41845600	-1.20481600	C	-0.66783900	3.45689900	-0.18694400
H	-1.43384000	4.25223500	-0.27937500	H	0.29339300	3.93935700	-0.39544400
C	-0.69188700	2.95326800	1.25829700	N	0.45329000	2.11057500	1.64363500
C	1.70115300	2.87260000	1.69398600	H	1.95620100	3.27492900	0.71006800
H	1.65200600	3.71591200	2.40962500	H	2.51726700	2.21182400	2.00419300
C	0.18234100	1.52085600	2.96236600	H	-0.69350000	0.87209700	2.88552000
H	1.04074300	0.91896700	3.27538800	H	0.00879000	2.29461600	3.73438600
H	-1.59410100	2.35942900	1.42902600	H	-0.75528700	3.83902300	1.92176400
C	-2.28530600	1.99217800	-1.24792900	H	-2.41026400	1.26917500	-2.05810200
H	-2.55772300	1.49096100	-0.31612200	H	-2.96661900	2.84657200	-1.42705600
C	-0.47914200	2.92002700	-2.52017200	H	0.58420100	3.18430900	-2.51494200
H	-0.63781200	2.14165100	-3.27277600	H	-1.05323100	3.81461900	-2.82940700
N	2.12144100	-0.49514300	-1.45052800	C	2.74898700	-1.81211000	-1.16889400
C	2.76025200	-2.16189100	0.34431900	N	1.42233700	-2.02592300	0.96733800
C	0.46835900	-3.08669300	0.61253800	H	0.35143200	-3.15022200	-0.47183400
H	0.75905600	-4.07780100	1.00138300	H	-0.50847300	-2.83594000	1.03516800
C	1.49675500	-1.90289300	2.42445300	H	2.19182100	-1.10035300	2.69492700
H	0.50522000	-1.64527000	2.80819400	H	1.82779000	-2.82762100	2.93131700
H	3.39261800	-1.41619800	0.84776000	C	3.41772400	-3.54739000	0.56883800
C	4.82464500	-3.65191000	-0.03097700	C	4.78564500	-3.34102100	-1.53039800
C	4.16976100	-1.95730000	-1.76881500	H	4.83240000	-1.20590800	-1.31834200
H	4.13638500	-1.73834600	-2.84298500	H	5.79300200	-3.38167200	-1.96392200
H	4.19075000	-4.10850700	-2.04699000	H	5.49949000	-2.94293500	0.47146800
H	5.23482400	-4.65383100	0.14830600	H	3.44756300	-3.76643100	1.64292200
H	2.79034800	-4.32289900	0.11067300	H	2.10534100	-2.54797700	-1.66770700
C	2.96938000	0.66012600	-1.14867700	H	2.36323000	1.56982600	-1.21577300
H	3.35636400	0.59338600	-0.12738800	H	3.82506000	0.77737500	-1.83625000
C	1.61448900	-0.41539400	-2.82388800	H	0.88023500	-1.20718200	-2.99114800
H	1.10249900	0.54168400	-2.95901900	H	2.40707600	-0.48347800	-3.59107800

Table A.2.14. 4a with TMEDA and (*R*,*R*)-TMCDA at –78 °C.

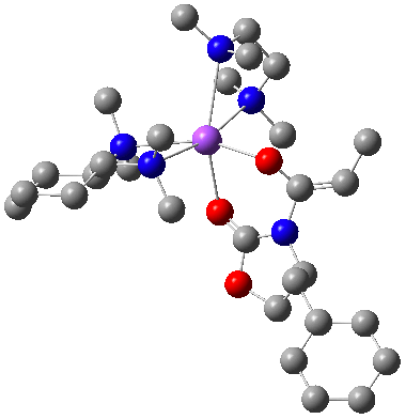




TMEDA



(*R*,*R*)-TMCDA

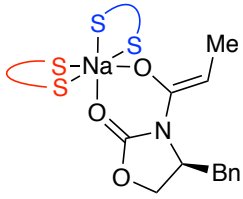


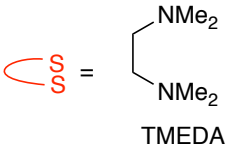
G = –1792.331233
G_{MP2} = –1791.574674

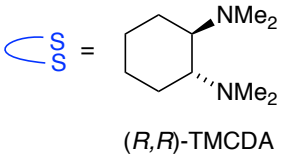
Na	0.00000000	0.00000000	0.00000000	O	-1.95531400	-0.73205900	0.86321000
C	-3.01451900	-1.09029900	0.23823700	N	-3.52292700	-0.13118300	-0.78184900
C	-2.73232000	0.67018500	-1.54076100	O	-3.50080700	1.57583900	-2.22961100
C	-4.88483100	1.21717700	-2.07317400	H	-5.47216500	2.13111000	-1.96322600
H	-5.21102000	0.68690300	-2.97553100	C	-4.91884500	0.31202200	-0.82851300
H	-5.58590800	-0.53812000	-0.99253800	C	-5.33809000	1.03074700	0.47581300
H	-5.08786000	0.35565500	1.30203500	H	-4.72570100	1.93326200	0.59174600
C	-6.80873900	1.38059100	0.50974000	C	-7.25131900	2.69652800	0.31990800
C	-8.61337600	3.00579200	0.32795100	C	-9.55837500	1.99882000	0.52544900
C	-9.13178200	0.68256800	0.71898200	C	-7.77095400	0.37875200	0.71182600
H	-7.44511000	-0.64644600	0.87557600	H	-9.86032400	-0.10759900	0.88191400
H	-10.6186750	2.23704500	0.53409600	H	-8.93407500	4.03441200	0.18377200
H	-6.52016600	3.48965000	0.17680700	O	-1.51367200	0.67355600	-1.67179500
C	-3.78159000	-2.20853200	0.39376400	H	-4.61546600	-2.37806100	-0.28161200
C	-3.51687800	-3.23730100	1.45630000	H	-4.43934000	-3.53454500	1.97703100
H	-3.07344300	-4.16769800	1.06397900	H	-2.82639400	-2.84056600	2.20830300
N	0.55843600	-2.27252700	-1.26270900	C	1.74511900	-2.39131500	-2.11044000
H	1.89159600	-3.42181100	-2.48822200	H	1.63802900	-1.72886200	-2.97474900
H	2.64922900	-2.09396600	-1.57137200	C	-0.64047700	-2.52957400	-2.07380100
H	-0.72188000	-1.76779700	-2.85419300	H	-0.60653400	-3.52747000	-2.55129500
H	-1.53353800	-2.47326700	-1.44693500	C	0.59497400	-3.20855000	-0.12817900
H	-0.38354000	-3.16314100	0.35857700	H	0.73120100	-4.24862500	-0.48684000
C	1.69536900	-2.92591300	0.89832400	H	2.66309300	-2.85369700	0.39075900
H	1.76708600	-3.80566500	1.56735300	N	1.50576600	-1.69738400	1.68541200

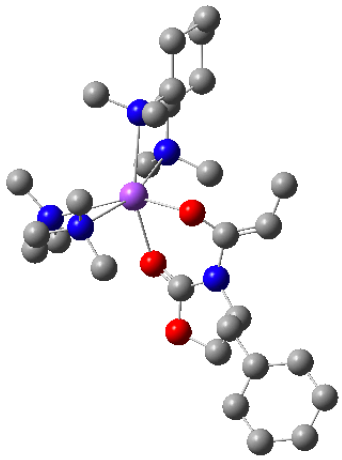
C	2.76690500	-1.31547700	2.32252000	H	2.62561700	-0.39207700	2.89345900
H	3.14909400	-2.08865800	3.01627500	H	3.53196500	-1.13259600	1.56062900
C	0.46409800	-1.88218900	2.70697400	H	0.42830400	-0.99491200	3.34501100
H	-0.51725700	-1.98136600	2.23860500	H	0.67072000	-2.75985800	3.34870200
N	1.69416800	1.77957400	-0.95697300	C	1.35234700	3.15647500	-0.51418100
C	1.01514800	3.23667200	1.00021700	N	-0.00977000	2.24668100	1.40539400
C	0.05267800	1.92728900	2.83143000	H	-0.20983100	2.77725500	3.48844400
H	-0.64913400	1.11391700	3.03985500	H	1.06157300	1.59228600	3.09736400
C	-1.38932600	2.60129400	1.04423000	H	-1.44712800	2.87493400	-0.01184400
H	-2.01310900	1.71548100	1.19500000	H	-1.79437400	3.43136000	1.64902100
H	1.92430600	2.96008500	1.55265400	C	0.66372400	4.69237400	1.39863500
C	1.75521300	5.70153300	1.02421200	C	2.04394300	5.63463400	-0.47815600
C	2.43154600	4.20703400	-0.88106900	H	3.37323100	3.95212700	-0.37564000
H	2.63451800	4.16237400	-1.95760800	H	2.84589100	6.33174000	-0.75257300
H	1.15025800	5.94945800	-1.03661200	H	2.67683000	5.48185500	1.58353100
H	1.44636700	6.71316100	1.31678600	H	-0.26629000	4.98785600	0.89541100
H	0.46069600	4.73398300	2.47578700	H	0.43924700	3.41354000	-1.06661600
C	3.01803300	1.31558100	-0.53977400	H	3.15043800	1.45472800	0.53687200
H	3.09889900	0.24290900	-0.74690900	H	3.85208800	1.81849000	-1.05973800
C	1.52210700	1.61419900	-2.40365700	H	1.70595100	0.56745700	-2.66633600
H	0.49046200	1.84703500	-2.67710700	H	2.21246700	2.23332200	-3.00417700

Table A.2.15. 4a with (*R*,*R*)-TMCDA and TMEDA at –78 °C.









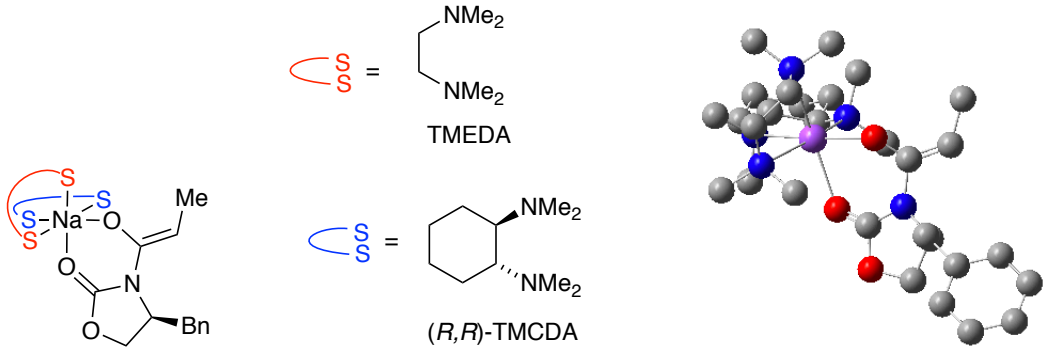
G = –1792.328352

G_{MP2} = –1791.572251

Na	0.00000000	0.00000000	0.00000000	O	-1.55576500	-1.42783300	0.78802400
C	-2.39925300	-2.12462900	0.12709100	N	-3.21783000	-1.37489000	-0.87387800
C	-2.78719700	-0.28613500	-1.55695300	O	-3.82996100	0.29369500	-2.23510500
C	-4.96740600	-0.58436300	-2.16407200	H	-5.86754800	0.02019500	-2.03570900
H	-5.03790600	-1.13753800	-3.10783600	C	-4.67415800	-1.51211800	-0.97121000
H	-4.94380800	-2.54292400	-1.21469800	C	-5.38171400	-1.10776000	0.34366000
H	-4.90470400	-1.68102400	1.14645600	H	-5.18767300	-0.04540600	0.53649900
C	-6.86940700	-1.37715000	0.31619300	C	-7.79824000	-0.33899600	0.16363400
C	-9.16900700	-0.60199200	0.11038400	C	-9.63423600	-1.91342400	0.20864400
C	-8.72006000	-2.95831000	0.36506600	C	-7.35263700	-2.69096300	0.41909600
H	-6.64681100	-3.50806000	0.55350500	H	-9.07347500	-3.98269300	0.45115600
H	-10.7003640	-2.12051900	0.16936300	H	-9.87195300	0.21932400	-0.00377800
H	-7.44438800	0.68796900	0.09802900	O	-1.66136800	0.19844800	-1.64085400
C	-2.70042400	-3.45173600	0.22501300	H	-3.40214800	-3.89521200	-0.47569800
C	-2.06117500	-4.34773800	1.24795700	H	-2.79105300	-5.02941800	1.70896500
H	-1.26289700	-4.98726200	0.83417600	H	-1.61224800	-3.75046200	2.04921900
N	0.73718400	2.58849000	-0.88429400	C	2.08821700	3.03957500	-0.54991700
H	2.25424400	3.00203700	0.53012900	H	2.82092900	2.37733400	-1.02220000
H	2.28595600	4.07347500	-0.89332200	C	0.55452900	2.59535800	-2.34042800
H	1.34131000	1.99779000	-2.80898700	H	-0.41085800	2.14624700	-2.58585500
H	0.60339200	3.61639800	-2.76458600	C	-0.28866600	3.43840200	-0.26132900
C	-0.43948200	3.25867000	1.25159700	N	-0.93155400	1.93550400	1.65148800
C	-0.71965700	1.72027400	3.08314500	H	-1.25813100	2.45929900	3.70709800
H	-1.07410100	0.72177800	3.35403200	H	0.34751100	1.78897800	3.32136200
C	-2.35798100	1.76111800	1.34927000	H	-2.54736200	1.94518300	0.29008800
H	-2.63174900	0.72352300	1.55583700	H	-2.99040000	2.44667500	1.94543900
H	0.52917400	3.41642900	1.73960700	H	-1.10547200	4.06195600	1.62466300
H	-1.23936300	3.21131200	-0.75226000	H	-0.08154600	4.50902500	-0.45904300
N	1.55448600	-1.53772100	-1.56877300	C	1.91716200	-0.87045200	-2.81822900
H	2.29911400	-1.55679100	-3.59643100	H	1.03215300	-0.37012300	-3.22296900
H	2.68581900	-0.11271400	-2.62783900	C	0.46866200	-2.49779200	-1.81455200
H	-0.39969700	-1.94769800	-2.18413600	H	0.73055600	-3.26873500	-2.55936100
H	0.16466300	-2.98574900	-0.88656500	C	2.73555000	-2.10446100	-0.87442300
H	3.51933500	-1.33757000	-0.95764300	C	2.48023200	-2.34236500	0.63811800
N	1.95065900	-1.13998200	1.33266900	C	2.94857400	-0.10477000	1.60487800
H	2.43435600	0.80332600	1.93934500	H	3.67917400	-0.37890200	2.38565000
H	3.49918300	0.14395200	0.69243800	C	1.22682900	-1.50558200	2.55619500
H	0.86121600	-0.59492600	3.03826800	H	0.35539100	-2.10957700	2.29177300
H	1.85068900	-2.04270300	3.29275300	H	1.68284900	-3.09153400	0.72091400

C	3.74660600	-2.92888000	1.31178700	H	4.55217400	-2.18240200	1.28078300
H	3.54122500	-3.12065700	2.37155900	C	4.25482200	-4.20686400	0.63410200
C	4.53819700	-3.94256000	-0.84739500	C	3.28288500	-3.39506200	-1.53618900
H	2.50751800	-4.17140900	-1.50434200	H	3.48665200	-3.20268400	-2.59652400
H	5.36212900	-3.21905800	-0.93890500	H	4.87080000	-4.85953400	-1.35025000
H	5.15612300	-4.56829300	1.14545800	H	3.50154700	-5.00287900	0.72579700

Table A.2.16. 4b with TMEDA and (*R*,*R*)-TMCDA at –78 °C.



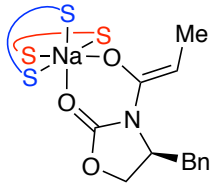
G = –1792.330851

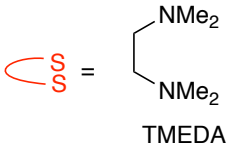
G_{MP2} = –1791.573696

Na	0.00000000	0.00000000	0.00000000	O	-1.86926100	-0.24195900	1.24414300
C	-2.68148500	-1.23374500	1.23376100	N	-3.21443600	-1.62212400	-0.10057900
C	-2.53204700	-1.49551400	-1.26910000	O	-3.36305900	-1.76015700	-2.33009300
C	-4.59521300	-2.30080200	-1.82433400	H	-5.42046900	-1.90691000	-2.42098700
H	-4.56555200	-3.39189100	-1.92800200	C	-4.63853700	-1.86461000	-0.34923300
H	-5.00391600	-2.68100600	0.27868300	C	-5.49406100	-0.60430300	-0.07912000
H	-5.24992000	-0.26907600	0.93515700	H	-5.18211100	0.18676400	-0.77201200
C	-6.97828400	-0.86390200	-0.20608800	C	-7.70193500	-0.43174300	-1.32567100
C	-9.06655200	-0.70272300	-1.44893600	C	-9.73160500	-1.41413700	-0.45009300
C	-9.02396500	-1.84805100	0.67368100	C	-7.66192200	-1.57413100	0.79311100
H	-7.11925400	-1.90529900	1.67621500	H	-9.53537100	-2.39581700	1.46114200
H	-10.7937080	-1.62489500	-0.54268400	H	-9.60903800	-0.35399700	-2.32402300
H	-7.19319300	0.13353900	-2.10390200	O	-1.35948800	-1.20237300	-1.46972700
C	-3.16348700	-1.96869000	2.27741600	H	-3.79607200	-2.82877800	2.07666800
C	-2.83160000	-1.66049900	3.71014100	H	-3.71780600	-1.72789200	4.35806200
H	-2.08203900	-2.34487600	4.14141700	H	-2.43107800	-0.64524800	3.80143000
N	-0.86606900	2.39613400	-1.16428400	C	-0.63249000	3.43207400	-0.14740600

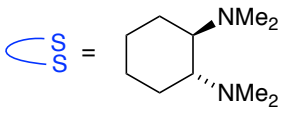
H	-1.38425600	4.24070400	-0.23981300	H	0.33694200	3.89652900	-0.35846200
C	-0.66308900	2.93071700	1.29966300	N	0.48077800	2.08879400	1.69180800
C	1.72513900	2.85525300	1.75712800	H	1.98901100	3.26121500	0.77726600
H	1.66485300	3.69568700	2.47545400	H	2.54053000	2.19686400	2.07483100
C	0.20293000	1.49032400	3.00516400	H	-0.67599100	0.84682600	2.92049100
H	1.05850700	0.88211900	3.31634800	H	0.03070200	2.25827900	3.78324500
H	-1.56569000	2.33668100	1.46664100	H	-0.72927500	3.81768600	1.96119400
C	-2.28064200	1.99882300	-1.20381700	H	-2.42308300	1.28129300	-2.01589800
H	-2.55942100	1.50113900	-0.27227600	H	-2.94392500	2.86794200	-1.37895600
C	-0.46222500	2.88591700	-2.48351400	H	0.59993600	3.15356100	-2.47874800
H	-0.61618600	2.09908100	-3.22871700	H	-1.03723700	3.77621800	-2.80276600
N	2.31791100	-0.28163600	-1.20956000	C	2.98570800	1.01780000	-1.28323400
H	2.25010300	1.78300200	-1.55095600	H	3.40335100	1.27698400	-0.30528200
H	3.79965700	1.06034000	-2.02940500	C	1.74618000	-0.63036400	-2.51643300
H	1.20251100	-1.57490500	-2.45788000	H	1.02007400	0.13757800	-2.79976000
H	2.49886700	-0.69451400	-3.32086800	C	3.19347100	-1.32493800	-0.61743800
H	3.62512600	-0.85967800	0.28064600	C	2.40592500	-2.58109900	-0.15703100
N	1.22941700	-2.24997700	0.67713600	C	0.21245800	-3.30601000	0.63804700
H	-0.09423400	-3.47756500	-0.39770700	H	0.56102100	-4.26238000	1.06965600
H	-0.66886500	-2.98263400	1.19960900	C	1.53462800	-1.89278400	2.06418000
H	2.29331400	-1.10353100	2.09718200	H	0.62218000	-1.50840400	2.53005000
H	1.89429800	-2.74052000	2.67367200	H	1.99493000	-3.05386700	-1.05875500
C	3.37151100	-3.60501700	0.49126200	H	3.79433700	-3.17618600	1.40995300
H	2.80599000	-4.49408800	0.79464000	C	4.52699400	-4.00267700	-0.43496300
H	5.18657100	-4.71791400	0.07270800	H	4.13117900	-4.51743600	-1.32283800
C	5.30958100	-2.76126100	-0.87370500	H	5.79356300	-2.30697000	0.00372100
H	6.11462800	-3.03329400	-1.56804800	C	4.37226600	-1.74196400	-1.53305800
H	3.97425300	-2.18323600	-2.45659100	H	4.93900900	-0.85228400	-1.83253600

Table A.2.17. 4b with (*R*,*R*)-TMCDA and TMEDA at –78 °C.

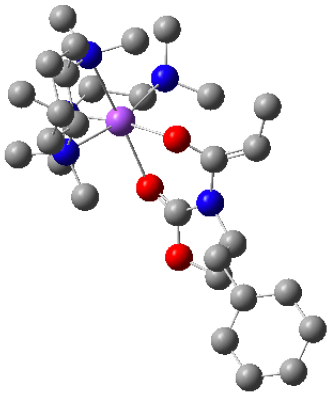




TMEDA



(*R,R*)-TMCDA



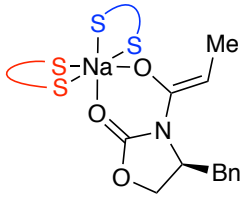
G = –1792.328122

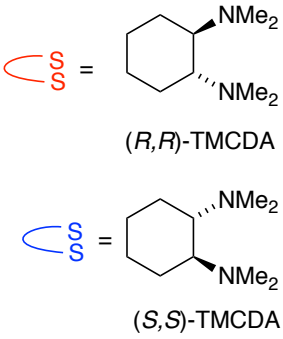
G_{MP2} = –1791.571598

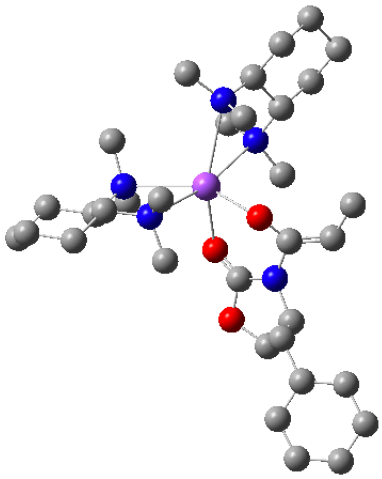
Na	0.00000000	0.00000000	0.00000000	O	-1.77738200	0.77415000	1.18363600
C	-2.82825100	0.15328000	1.56760900	N	-3.56061300	-0.59191200	0.49999300
C	-2.96725300	-1.15678600	-0.58098200	O	-3.91598800	-1.58674100	-1.47381200
C	-5.20931200	-1.48273000	-0.85251300	H	-5.93001200	-1.14538600	-1.60010500
H	-5.50272000	-2.47582700	-0.49254400	C	-5.00963900	-0.48672500	0.30345100
H	-5.54296800	-0.82485600	1.19540600	C	-5.44239700	0.96322700	-0.01932600
H	-5.03431700	1.59754700	0.77557400	H	-4.96939700	1.26854500	-0.96076500
C	-6.94344800	1.12399700	-0.10434600	C	-7.59655200	1.24234700	-1.33858000
C	-8.98651100	1.36067000	-1.40858500	C	-9.74845900	1.36151900	-0.24003100
C	-9.11079200	1.24795300	0.99785600	C	-7.72278000	1.13120200	1.06306200
H	-7.23161400	1.05428900	2.03099000	H	-9.69534900	1.25605500	1.91432200
H	-10.8299460	1.45524400	-0.29169900	H	-9.47188100	1.45608900	-2.37658100
H	-7.00852400	1.25434800	-2.25409400	O	-1.77571400	-1.32629500	-0.82462200
C	-3.41143000	0.09696600	2.79902800	H	-4.27584700	-0.54358600	2.95048700
C	-2.88512700	0.85741600	3.98264100	H	-3.67908500	1.41307800	4.50466000
H	-2.41603500	0.20849800	4.74074600	H	-2.12845600	1.58162700	3.66320600
N	-0.20694100	2.15154900	-1.43294200	C	-1.60056100	1.96118900	-1.85245500
H	-1.67290800	1.03824300	-2.43809100	H	-2.21896700	1.84368000	-0.95964100
H	-1.99061900	2.78697100	-2.47367700	C	0.66270100	2.24503800	-2.60451900
H	1.71068800	2.33777800	-2.30551900	H	0.56243200	1.32386500	-3.18913800
H	0.41965300	3.08643300	-3.27729000	C	-0.06896800	3.26108900	-0.45129300
C	1.31148300	3.26079100	0.26192200	N	1.64805000	1.94933700	0.88080400
C	3.09037300	1.71238800	0.89675900	H	3.49465600	1.78185300	-0.11859900
H	3.65076500	2.41704700	1.53966300	H	3.28615000	0.70129500	1.27114000
C	1.08697300	1.74452100	2.22421000	H	0.00157700	1.86461900	2.20665400
H	1.28713700	0.71087200	2.52444400	H	1.52974700	2.40367700	2.99020200
H	2.07516000	3.42418700	-0.51004300	C	1.41728100	4.44727700	1.25182000

H	2.40937400	4.44000400	1.72105300	H	0.68781300	4.30951600	2.05989600
C	1.15025300	5.80503300	0.59396600	H	1.23013000	6.60478300	1.34132600
H	1.91586200	6.01105200	-0.16898400	C	-0.23452500	5.80465600	-0.05823500
H	-1.00359100	5.69191900	0.71961400	H	-0.43129600	6.76231700	-0.55711200
C	-0.34688000	4.65666400	-1.06814200	H	0.36940800	4.84323400	-1.88068000
H	-1.34286800	4.66051200	-1.52507800	H	-0.83524600	3.05540400	0.30649600
N	0.72186400	-2.19221100	1.40165200	C	-0.52485400	-2.56100500	2.08527300
H	-1.33959200	-2.58764800	1.36050700	H	-0.45072300	-3.54755300	2.58102600
H	-0.77298100	-1.80622400	2.83605400	C	1.81367900	-2.14865200	2.37539200
H	2.73664300	-1.78223800	1.91640800	H	1.54962000	-1.46516300	3.18804000
H	2.02024000	-3.14177000	2.81912500	C	1.00123000	-3.14192700	0.31353800
H	0.06698100	-3.29378200	-0.23415900	H	1.29857600	-4.12839500	0.72183300
C	2.09323000	-2.68361300	-0.65728700	N	1.70913300	-1.55332300	-1.51802700
C	2.90651800	-0.92036200	-2.07535000	H	2.61591600	-0.07045500	-2.69948500
H	3.54238000	-0.54852600	-1.26601900	H	3.50514600	-1.61316800	-2.69717600
C	0.82906500	-1.99284600	-2.60883400	H	-0.11257200	-2.37480600	-2.21329800
H	0.58737700	-1.13588700	-3.24535100	H	1.30822400	-2.76676900	-3.23827200
H	2.98325800	-2.38684700	-0.09261800	H	2.39631300	-3.55376100	-1.27137700

Table A.2.18. 4a with (*S*,*S*)-TMCDA and (*R*,*R*)-TMCDA at –78 °C.







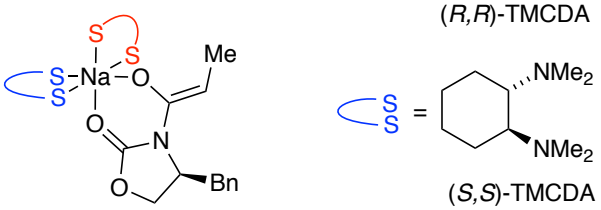
G = –1947.826333
G_{MP2} = –1946.976201

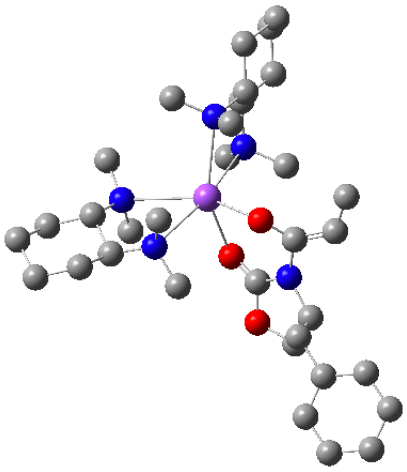
Na	0.00000000	0.00000000	0.00000000	O	1.64695400	-1.15654000	-1.00285300
C	2.54052600	-1.87041700	-0.43009600	N	3.33702700	-1.18733400	0.62996300

C	2.85890900	-0.20865600	1.44012000	O	3.88363700	0.35164900	2.16087600
C	5.06783400	-0.44150800	1.96860100	H	5.92803200	0.22730000	1.89742200
H	5.19314100	-1.09584300	2.83926400	C	4.80110200	-1.24060000	0.68039400
H	5.14233700	-2.27272400	0.79363800	C	5.44401100	-0.63901200	-0.59160600
H	4.98687800	-1.14899000	-1.44695800	H	5.17066800	0.42140000	-0.65612700
C	6.94690200	-0.80243700	-0.62304400	C	7.80497300	0.27319000	-0.35774400
C	9.19153600	0.10496500	-0.36048100	C	9.74383200	-1.14762400	-0.62893400
C	8.90072400	-2.22858000	-0.89850200	C	7.51714400	-2.05569700	-0.89592000
H	6.86620800	-2.89889900	-1.11801900	H	9.32211500	-3.20656500	-1.11685600
H	10.8224010	-1.28080700	-0.63362900	H	9.83864200	0.95433300	-0.15671500
H	7.38220000	1.25598900	-0.15915500	O	1.71040000	0.19343800	1.59630000
C	2.90935500	-3.16221300	-0.67386100	H	3.65400100	-3.63399500	-0.03891200
C	2.31173700	-3.97519000	-1.78711700	H	3.07953900	-4.52423700	-2.35230300
H	1.58850700	-4.73229600	-1.43917300	H	1.78455200	-3.32248500	-2.49132400
N	-1.15658500	-2.08295700	1.27535600	C	-2.11937400	-1.56238600	2.24630600
H	-2.48693500	-2.31885900	2.96185500	H	-1.63314800	-0.77580100	2.83200600
H	-2.98419900	-1.12238900	1.74062500	C	0.01845100	-2.61379400	1.98015100
H	0.50019200	-1.79760100	2.52551900	H	-0.23191000	-3.41173000	2.70184800
H	0.74150700	-3.00258500	1.25715100	C	-1.71813700	-3.06512000	0.31316800
H	-0.85643600	-3.41432400	-0.2699120	C	-2.72946100	-2.42934800	-0.67848000
H	-3.58490700	-2.07187300	-0.08887700	N	-2.19415500	-1.22459500	-1.36544000
C	-3.26691000	-0.35743800	-1.85163300	H	-2.83223700	0.56880100	-2.24377300
H	-3.87348600	-0.80517900	-2.66016800	H	-3.93954100	-0.09290700	-1.02877000
C	-1.25358900	-1.52125500	-2.45483600	H	-0.86467000	-0.57707000	-2.84360100
H	-0.39468300	-2.08344500	-2.08325600	H	-1.71580800	-2.05872500	-3.30006100
C	-3.27324700	-3.50376300	-1.65535000	H	-3.99819200	-3.04202200	-2.33696900
H	-2.45013100	-3.87460700	-2.27906800	C	-3.90681000	-4.70082300	-0.93850700
H	-4.27014200	-5.42909700	-1.67473700	H	-4.78477500	-4.37205200	-0.36248000
C	-2.88731000	-5.34218500	0.00621100	C	-2.35529200	-4.30228900	0.99913800
H	-1.61937700	-4.76556900	1.66563500	H	-3.18999000	-3.97595100	1.63470900
H	-3.33436200	-6.18412300	0.55011100	H	-2.05501700	-5.75513200	-0.58210700
N	-0.97851800	2.35421700	0.97597400	C	-0.30297300	3.54870600	0.40378800
C	-0.04701000	3.42955500	-1.12342000	N	0.64284500	2.17023800	-1.48554800
C	0.49575800	1.83826500	-2.90281300	H	1.01408600	2.54127900	-3.58043200
H	0.91477500	0.84184100	-3.07281200	H	-0.56528800	1.82536700	-3.17771400
C	2.06643600	2.11794500	-1.12171600	H	2.20046500	2.37409400	-0.06820800
H	2.40561000	1.08774100	-1.26080000	H	2.69362900	2.78958600	-1.73369400
H	-1.02823600	3.37879900	-1.61802000	C	0.66617100	4.70237500	-1.64894600
C	-0.08042200	5.99842000	-1.31320300	C	-0.28865200	6.11291700	0.19929700
C	-1.03053600	4.87913500	0.72573900	H	-2.03243900	4.86291600	0.27562900

H	-1.17808200	4.96211900	1.80912300	H	-0.85035400	7.02225600	0.44836900
H	0.68818100	6.20147100	0.69705400	H	-1.05785300	6.00888600	-1.81814400
H	0.47772300	6.86217000	-1.69637700	H	1.67070600	4.75820400	-1.20961400
H	0.80650600	4.61840700	-2.73329700	H	0.67681700	3.58406700	0.89658900
C	-2.41245300	2.27619000	0.69122600	H	-2.59425700	2.39697900	-0.38029300
H	-2.77837900	1.28503200	0.97910200	H	-3.01738500	3.02544800	1.23123800
C	-0.73071300	2.23864800	2.41666900	H	-1.22039700	1.33534300	2.79308700
H	0.34156100	2.13239100	2.59616200	H	-1.12081600	3.09087300	3.00159200

Table A.2.19. 4a with (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA at –78 °C.



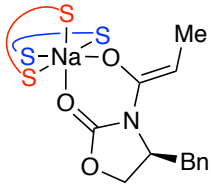


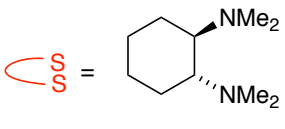
G = –1947.826796
G_{MP2} = –1946.977177

Na	0.00000000	0.00000000	0.00000000	O	1.69945200	-1.00390700	-1.07507100
C	2.63693200	-1.72665200	-0.58944900	N	3.36786100	-1.14743600	0.57661800
C	2.81772300	-0.30837600	1.49143000	O	3.79188300	0.20250500	2.31223000
C	5.02003400	-0.50284700	2.06280400	H	5.84625800	0.20998700	2.10230300
H	5.15576600	-1.25308600	2.85052200	C	4.83065000	-1.14756600	0.67765500
H	5.21251100	-2.17160600	0.67990700	C	5.49156400	-0.37045000	-0.48522800
H	5.08270700	-0.78563700	-1.41320200	H	5.18042600	0.67976700	-0.42816100
C	6.99989100	-0.47558100	-0.47926400	C	7.80502200	0.58903000	-0.05232400
C	9.19656900	0.47246500	-0.02344000	C	9.80747900	-0.71654400	-0.42232400
C	9.01779500	-1.78520900	-0.85392600	C	7.62898600	-1.66387800	-0.88231800
H	7.02056300	-2.49561000	-1.23152000	H	9.48515000	-2.71269400	-1.17495100
H	10.8901170	-0.80924800	-0.40280000	H	9.80175900	1.31284900	0.30705500

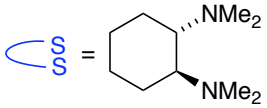
H	7.33694300	1.52384800	0.24961700	O	1.64539500	0.01035800	1.66518900
C	3.10187800	-2.93834100	-1.00972000	H	3.86244000	-3.45233300	-0.42924100
C	2.56381700	-3.62286600	-2.23469300	H	3.35944900	-4.12757100	-2.80125000
H	1.80724300	-4.39484000	-2.01183800	H	2.09080300	-2.89447500	-2.90308400
N	0.88404400	2.35513000	-1.01477800	C	0.32194400	3.62516500	-0.50980400
C	-1.16009400	3.49336200	-0.06928600	N	-1.39125500	2.33124500	0.82743900
C	-2.81623400	2.09837100	1.06225700	H	-3.35581600	2.10485200	0.10999600
H	-2.95032400	1.11358400	1.52258600	H	-3.28891600	2.84200700	1.72815100
C	-0.67368500	2.39167900	2.10641800	H	-0.89153900	1.48124800	2.67223500
H	0.40502100	2.41098200	1.94444200	H	-0.96378000	3.25147800	2.73498400
C	-1.65867100	4.84374900	0.50870100	C	-1.47052800	6.01648600	-0.46262000
C	-0.00311400	6.14259000	-0.88194100	C	0.49229400	4.82090600	-1.47933100
H	1.54782700	4.90417400	-1.76532300	H	-0.06693800	4.62507700	-2.40423200
H	0.12494000	6.95634000	-1.60704400	H	0.60597400	6.40597800	-0.00461700
H	-1.82429600	6.94564200	0.00198800	H	-2.09204900	5.85851400	-1.35664200
H	-2.71643700	4.76022100	0.78354100	H	-1.11290100	5.06600900	1.43571000
H	-1.75732600	3.28341900	-0.96939200	H	0.90422200	3.86203100	0.39012800
C	2.33921100	2.28283400	-0.86300900	H	2.61039800	2.46841500	0.18109900
H	2.65465600	1.26990100	-1.12570800	H	2.88233700	3.00488900	-1.50120100
C	0.51479200	2.01321400	-2.39004600	H	0.85568300	0.99286200	-2.58966700
H	-0.57280400	2.05113900	-2.51669600	H	0.96817800	2.67593000	-3.14862100
N	-1.86997100	-1.24976200	-1.51915800	C	-2.97821400	-0.31273700	-1.71266800
H	-2.57032900	0.67884400	-1.93796600	H	-3.65691000	-0.58763200	-2.53866900
H	-3.57066800	-0.22777900	-0.79757400	C	-1.12673200	-1.43271000	-2.77200100
H	-0.88616300	-0.45073200	-3.18964600	H	-0.18161300	-1.93907300	-2.56422400
H	-1.69439000	-1.98894400	-3.53959500	C	-2.26958900	-2.55721500	-0.93196900
C	-2.44193800	-2.49919200	0.61063700	N	-1.24125100	-1.95408900	1.29196700
C	-0.08173500	-2.85862800	1.30371700	H	0.18600500	-3.16360800	0.29047200
H	0.77190500	-2.31361200	1.70984100	H	-0.24073500	-3.75852000	1.92177200
C	-1.52520900	-1.50937700	2.65759700	H	-0.64891800	-0.97928900	3.04470300
H	-2.37771100	-0.82094000	2.65855100	H	-1.75410000	-2.33427100	3.35666400
H	-3.25013100	-1.78454800	0.82571200	C	-2.88672100	-3.88020100	1.15865000
H	-2.07198000	-4.60175800	1.01615000	H	-3.05010300	-3.80631300	2.24044000
C	-4.14042000	-4.43415400	0.47252700	C	-3.91306800	-4.53671700	-1.03804000
C	-3.52650200	-3.16538400	-1.60324400	H	-4.37882700	-2.48795700	-1.45969300
H	-3.36219200	-3.23343700	-2.68542000	H	-4.81258600	-4.90951800	-1.54432300
H	-3.11431700	-5.26521800	-1.23996300	H	-4.39660900	-5.41326900	0.89674600
H	-4.99848900	-3.77363500	0.66791600	H	-1.43068700	-3.23306900	-1.13818800

Table A.2.20. 4b with (*S*,*S*)-TMCDA and (*R*,*R*)-TMCDA at –78 °C.

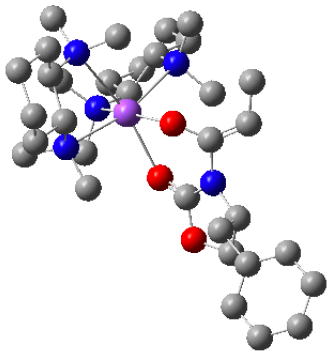




(*R*,*R*)-TMCDA



(*S*,*S*)-TMCDA

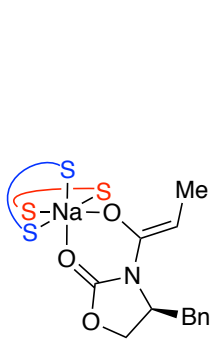


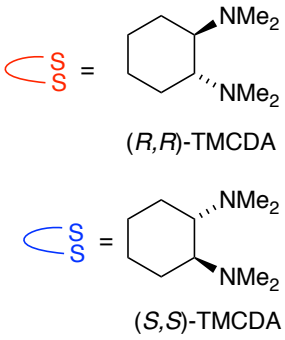
G = –1947.825274
G_{MP2} = –1946.975833

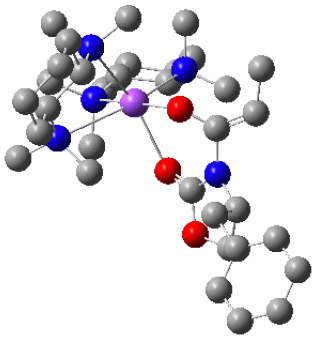
Na	0.00000000	0.00000000	0.00000000	O	-1.90357100	0.15445500	1.18586500
C	-2.69249500	-0.80929100	1.48135900	N	-3.22219000	-1.58657700	0.32447200
C	-2.53922900	-1.80679100	-0.82813000	O	-3.35846600	-2.39625000	-1.75780700
C	-4.58911800	-2.77129800	-1.11618300	H	-5.41509800	-2.57140400	-1.80187600
H	-4.55526700	-3.84540300	-0.89935400	C	-4.63920300	-1.92499200	0.16943500
H	-4.98150500	-2.53252800	1.01127100	C	-5.52655300	-0.66180300	0.07196200
H	-5.29049300	-0.04272000	0.94481500	H	-5.23573200	-0.09571000	-0.82161200
C	-7.00367400	-0.98355700	0.03716600	C	-7.73910200	-0.90932500	-1.15339100
C	-9.09627600	-1.23799100	-1.18257900	C	-9.74182100	-1.64890800	-0.01616000
C	-9.02231700	-1.72413500	1.17904300	C	-7.66785800	-1.39362200	1.20378100
H	-7.11648200	-1.44295400	2.14055700	H	-9.51869600	-2.03531200	2.09472800
H	-10.7981240	-1.90369900	-0.03560900	H	-9.64829300	-1.16890000	-2.11647900
H	-7.24544200	-0.57897700	-2.06509400	O	-1.36886400	-1.56828000	-1.10668800
C	-3.15083000	-1.21779400	2.70028200	H	-3.77541500	-2.10429900	2.76642800
C	-2.80730300	-0.50275900	3.97589500	H	-3.70072400	-0.26719200	4.57436400
H	-2.14403700	-1.08890400	4.63325700	H	-2.29726400	0.44059400	3.75526900
N	2.04249100	-1.05987300	-1.30737500	C	2.53733500	-2.33676700	-0.72853000
C	2.62412400	-2.30912300	0.82177900	N	1.35833900	-1.86960300	1.46037300
C	0.27587200	-2.86462500	1.41690800	H	0.07748000	-3.16814700	0.38706300
H	0.48912700	-3.76151400	2.02331200	H	-0.63848700	-2.40859700	1.80688700
C	1.56236600	-1.43892400	2.84504200	H	2.35120500	-0.67950100	2.88993300
H	0.63358300	-0.99811500	3.21963400	H	1.84137900	-2.26029400	3.52972600
H	3.36762800	-1.54662000	1.09559400	C	3.14474000	-3.66939500	1.35284800
C	4.48296400	-4.09089400	0.73524600	C	4.36288900	-4.15185800	-0.78975700
C	3.88697600	-2.80089700	-1.33537500	H	4.66013500	-2.05251700	-1.11460500
H	3.80012700	-2.84500500	-2.42755500	H	5.32307400	-4.42223200	-1.24724600

H	3.64901400	-4.94057500	-1.06906300	H	5.26753300	-3.37056400	1.01131000
H	4.79350400	-5.06185900	1.14155600	H	3.23115100	-3.62398900	2.44479900
H	2.40473900	-4.44933900	1.13168400	H	1.78086500	-3.08439400	-0.99869000
C	3.03161500	0.02073900	-1.32362900	H	2.52841600	0.95959700	-1.57661500
H	3.47825300	0.14262300	-0.33297700	H	3.84550500	-0.13131900	-2.05387500
C	1.47844700	-1.26002100	-2.64657000	H	0.64607600	-1.96504900	-2.59237500
H	1.08116800	-0.30819500	-3.01296800	H	2.21714200	-1.61549900	-3.38709300
N	0.97217700	2.54426700	0.98558900	C	2.40443900	2.80892200	1.10654700
H	2.82492200	3.06466700	0.12812300	H	2.65109100	3.62583100	1.81028500
H	2.90992500	1.90533600	1.46542900	C	0.42864600	2.11566500	2.28154900
H	-0.62375300	1.83771300	2.18720700	H	0.96855100	1.22050900	2.60125100
H	0.54701700	2.86964600	3.07884500	C	0.25131500	3.68737400	0.36725100
C	-1.04897300	3.26136700	-0.36749200	N	-0.82113800	2.17615200	-1.35941300
C	-2.08491300	1.58344900	-1.81447500	H	-1.86631100	0.69164100	-2.40974000
H	-2.65758000	1.26914300	-0.93868500	H	-2.69363200	2.26591500	-2.43384600
C	-0.00136500	2.55584500	-2.50946300	H	0.97235300	2.93543200	-2.18592300
H	0.17407000	1.66677700	-3.12406600	H	-0.46722400	3.31380500	-3.16357300
H	-1.72329300	2.81997100	0.37695800	C	-1.74603500	4.50660800	-0.97832800
H	-1.11846600	4.91544500	-1.78228500	H	-2.68931100	4.20269700	-1.44547600
C	-2.00885900	5.62527300	0.03658000	H	-2.48967600	6.47645900	-0.46246200
H	-2.71261500	5.27354700	0.80488600	C	-0.70030800	6.05255200	0.70527100
C	-0.03587200	4.83965000	1.36351600	H	-0.70098700	4.47562500	2.15662600
H	0.90022400	5.13680600	1.85280500	H	-0.88008800	6.83424900	1.45439800
H	-0.02737200	6.48805200	-0.04848600	H	0.93624400	4.08864800	-0.39152600

Table A.2.21. 4b with (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA at –78 °C.







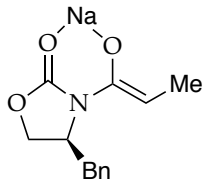
G = –1947.825101

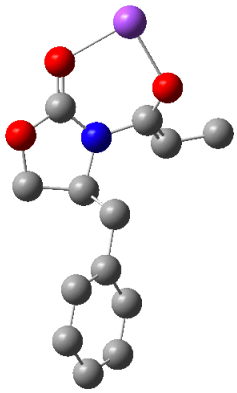
G_{MP2} = –1946.975146

Na	0.00000000	0.00000000	0.00000000	O	-1.92415900	-0.10640600	1.16071600
C	-2.66552900	-1.12883300	1.38047300	N	-3.07815500	-1.89652400	0.17297200
C	-2.31335700	-2.04140100	-0.93847100	O	-3.04071700	-2.63516600	-1.93915400
C	-4.29267600	-3.08553100	-1.39247800	H	-5.07931700	-2.90376200	-2.12760400
H	-4.22148500	-4.16270200	-1.20158600	C	-4.46719500	-2.28044400	-0.09229400
H	-4.84587900	-2.92311200	0.70664500	C	-5.38952500	-1.04511500	-0.22017000
H	-5.23747200	-0.44483600	0.68393200	H	-5.05516800	-0.44402900	-1.07484200
C	-6.84865200	-1.41247500	-0.36968400	C	-7.49893000	-1.33206900	-1.60849000
C	-8.83914200	-1.70168300	-1.74269400	C	-9.55291900	-2.16004100	-0.63520300
C	-8.91884300	-2.24185400	0.60704800	C	-7.58100100	-1.87069500	0.73659200
H	-7.09653500	-1.92568800	1.70936600	H	-9.46921100	-2.58981100	1.47749000
H	-10.5963450	-2.44642200	-0.73673100	H	-9.32494200	-1.62712200	-2.71230100
H	-6.95276900	-0.96419400	-2.47475100	O	-1.14160900	-1.73360800	-1.13159400
C	-3.16962300	-1.60219600	2.55568500	H	-3.72965900	-2.53332000	2.55637900
C	-2.95745000	-0.90820700	3.87103500	H	-3.89089400	-0.82561800	4.44774000
H	-2.23710400	-1.42743200	4.52465900	H	-2.57615000	0.10570000	3.71043400
N	2.27651900	-0.36356800	-1.30008500	C	2.90566700	0.92016400	-1.61480500
H	2.13507800	1.62406800	-1.94367300	H	3.38061600	1.33239700	-0.71911100
H	3.66915000	0.85692700	-2.41170500	C	1.62258200	-0.90292000	-2.50053900
H	1.13540200	-1.85390300	-2.28068500	H	0.83718900	-0.20894600	-2.81539100
H	2.31274600	-1.03374300	-3.35122100	C	3.22427600	-1.30272300	-0.64423600
H	3.78612000	-0.69129700	0.07570900	C	2.50412300	-2.41875700	0.16075900
N	1.50472100	-1.88167900	1.11703600	C	0.50744600	-2.89041100	1.49624900
H	0.05491000	-3.30766900	0.59380100	H	0.92971000	-3.71302000	2.10134700
H	-0.29028400	-2.41507000	2.07488800	C	2.07189800	-1.26707800	2.31859200
H	2.79896100	-0.49316100	2.05117000	H	1.26237800	-0.79289100	2.88162400
H	2.56707200	-1.98481300	2.99545100	H	1.92218500	-3.01265800	-0.55595800
C	3.54309600	-3.36644500	0.81331600	H	4.11224200	-2.81388800	1.57318900
H	3.01772100	-4.17020200	1.34259800	C	4.53896400	-3.95852300	-0.19078800
H	5.25314800	-4.60867900	0.33031000	H	4.00768200	-4.59346100	-0.91492100
C	5.26810100	-2.83726000	-0.93660600	H	5.87545400	-2.25915200	-0.22420400
H	5.96379000	-3.24924300	-1.67856400	C	4.25405300	-1.91715400	-1.62500600
H	3.72311900	-2.50276800	-2.38694900	H	4.77447000	-1.11227600	-2.15839600
N	-0.99347400	2.27385200	-1.75383100	C	-1.25521600	3.46132400	-0.90214000
H	-0.46290000	4.17973700	-1.15266400	C	-1.14283800	3.16627900	0.61982300
N	0.13708700	2.49705000	0.98930600	C	1.34044800	3.28820800	0.73410600
H	1.40352300	3.56931300	-0.32000600	H	1.41148400	4.20551400	1.34480300
H	2.21835300	2.67502700	0.96501500	C	0.12388900	2.03583700	2.38325700
H	-0.73815000	1.38027400	2.53276900	H	1.03566100	1.45764600	2.56990200

H	0.10541300	2.85424000	3.12385700	H	-1.91892300	2.43741000	0.88445900
C	-1.40213300	4.46950600	1.42242700	H	-1.37015600	4.25132200	2.49511200
H	-0.59290200	5.18699600	1.22579900	C	-2.73671000	5.14255600	1.07905900
C	-2.81465500	5.44532200	-0.41896300	C	-2.60175600	4.15787300	-1.22162900
H	-2.65439700	4.36759800	-2.29741200	H	-3.42760600	3.47146200	-0.99572300
H	-3.78254500	5.89369100	-0.67746000	H	-2.04482800	6.18507200	-0.68528400
H	-2.85492000	6.05986200	1.67006900	H	-3.56791000	4.47929600	1.35937500
C	-2.13731400	1.36406500	-1.89300300	H	-1.80340300	0.45501100	-2.40257800
H	-2.50471200	1.06880800	-0.90633200	H	-2.96767300	1.79236500	-2.48204000
C	-0.49126000	2.64993900	-3.07340600	H	0.41114500	3.26384000	-2.97482300
H	-0.22681600	1.74499500	-3.63162500	H	-1.22058100	3.21109600	-3.68767100

Table A.2.22. 2 at –78 °C.





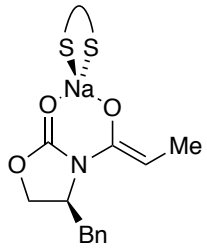
G = –943.7474627

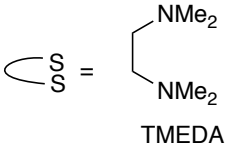
G_{MP2} = –943.5222257

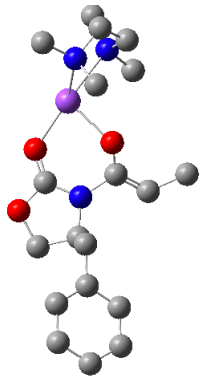
C	0.00000000	0.00000000	0.00000000	O	1.18017500	-0.70637600	-0.43182600
C	2.14058700	0.20809700	-0.74752200	N	1.62996000	1.46102200	-0.73748800
C	2.35042600	2.68299700	-1.19767700	C	2.08244800	3.80758500	-0.48290500
H	1.45745400	3.73747300	0.40319200	C	2.64361500	5.15001700	-0.85455000
H	1.85643800	5.90649700	-0.99623000	H	3.32307800	5.55074500	-0.08636900
H	3.20692700	5.07310400	-1.78963300	O	3.09829700	2.53515500	-2.23617200
Na	4.54213000	1.03633300	-2.27962100	O	3.29221700	-0.17053600	-0.98427300
C	0.17521500	1.42664500	-0.55066600	H	-0.12857500	2.16689700	0.19347000
C	-0.57780900	1.70256100	-1.87271600	H	-0.18341700	2.64261000	-2.27449100
H	-0.32954800	0.91133300	-2.59078200	C	-2.07549300	1.79717800	-1.68366300
C	-2.92540300	0.74616100	-2.05323600	C	-4.30426500	0.83014000	-1.84701300

C	-4.85632200	1.97136100	-1.26490200	C	-4.02148400	3.02871900	-0.89497000
C	-2.64556500	2.94109800	-1.10371700	H	-2.00268300	3.77330500	-0.82388600
H	-4.44358800	3.92550700	-0.44873800	H	-5.92908800	2.04015300	-1.10555600
H	-4.94582400	0.00518200	-2.14598000	H	-2.50416500	-0.14208800	-2.51971300
H	-0.87632200	-0.51785600	-0.39406300	H	-0.03024700	-0.01905900	1.09509300

Table A.2.23. 11 at –78 °C.







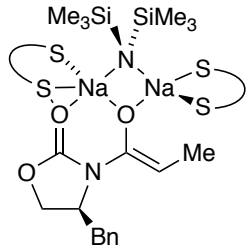
G = –1290.294396

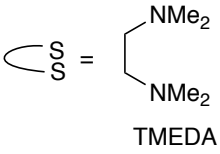
G_{MP2} = –1289.850469

Na	0.00000000	0.00000000	0.00000000	O	1.41962900	-1.10296800	-1.20598700
C	2.43912000	-1.75050200	-0.76959900	N	3.26313100	-1.05607500	0.25846400
C	2.78783300	-0.19054200	1.18990500	O	3.82311900	0.40395000	1.85839900
C	5.04700900	-0.25482300	1.48675500	H	5.83613400	0.49553500	1.40878800
H	5.30748900	-0.97237400	2.27349500	C	4.72302400	-0.95181700	0.15536900
H	5.17618500	-1.94538400	0.12219300	C	5.14985900	-0.15986600	-1.10308000
H	4.65075100	-0.63148800	-1.95695200	H	4.76377600	0.86372000	-1.02078000
C	6.64771200	-0.14620800	-1.31005800	C	7.41624000	0.98696500	-1.01143900
C	8.80290200	0.98019900	-1.17866000	C	9.44542500	-0.16561300	-1.64819500
C	8.69170300	-1.30180700	-1.95298900	C	7.30740300	-1.29011000	-1.78583000
H	6.72503600	-2.17465700	-2.03575700	H	9.18259600	-2.19665400	-2.32706300
H	10.5240150	-0.17293800	-1.78096500	H	9.37890800	1.87208600	-0.94537900
H	6.92152700	1.88860100	-0.65590900	O	1.62851300	0.09448500	1.48592400
C	2.90791800	-2.97159300	-1.15037100	H	3.75411200	-3.40736700	-0.62727400
C	2.27919700	-3.76408800	-2.26087100	H	3.02623900	-4.12930900	-2.98186500
H	1.73534600	-4.65391300	-1.90422600	H	1.56432600	-3.14068000	-2.80855000
N	-1.98775300	-1.39354800	-0.39006700	C	-3.23550800	-1.31188600	0.37290800

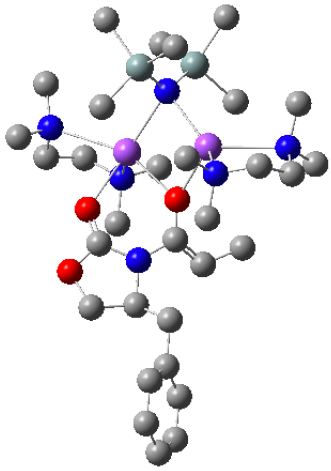
H	-4.01434100	-1.98906300	-0.02377900	H	-3.04187600	-1.58597900	1.41462400
H	-3.63193600	-0.29261500	0.36473000	C	-1.42220100	-2.74995000	-0.29775700
H	-1.28300200	-3.01303100	0.75599700	H	-2.08118100	-3.50790300	-0.75821700
H	-0.44615100	-2.76534400	-0.79020300	C	-2.17298300	-1.01941300	-1.80449000
H	-1.27770700	-1.34337500	-2.34432600	H	-3.02873900	-1.56524800	-2.24528200
C	-2.39549900	0.48136300	-2.03058300	H	-3.22130300	0.82893400	-1.40109300
H	-2.72096300	0.62854300	-3.07713000	N	-1.21879000	1.31902900	-1.73103800
C	-1.62098400	2.71382000	-1.51914000	H	-0.74080300	3.31387400	-1.26744800
H	-2.09592700	3.15995300	-2.41173100	H	-2.32852500	2.77619100	-0.68572100
C	-0.21617900	1.24173400	-2.80844000	H	0.61291900	1.91655600	-2.57469900
H	0.20128200	0.23488600	-2.87669400	H	-0.64253300	1.53750500	-3.78420200

Table A.2.24. 6a with TMEDA at –78 °C.





TMEDA



G = –2669.984607

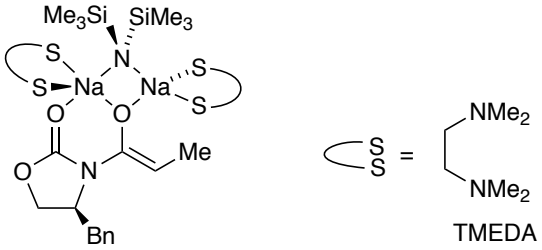
G_{MP2} = –2669.100098

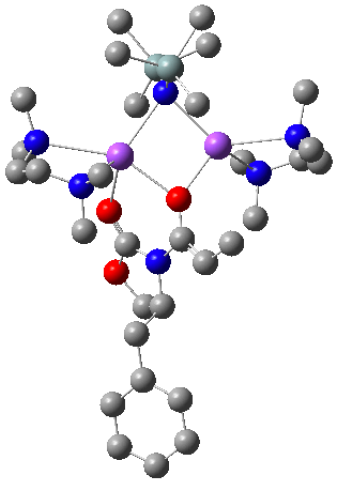
Na	0.00000000	0.00000000	0.00000000	O	-1.94008200	-0.80476400	-1.04180900
C	-3.10723600	-0.46569600	-0.91851400	O	-4.07451800	-1.04083700	-1.69302900
C	-5.33286300	-0.40496500	-1.42522300	C	-5.13186900	0.33756600	-0.09218700
N	-3.66653800	0.44112500	-0.05925100	C	-2.88622100	1.08323200	1.01841500
C	-3.48506100	1.18287600	2.23957200	H	-4.46610400	0.74488200	2.39676700
C	-2.82817800	1.84919700	3.41579600	H	-2.73829600	1.17469400	4.28079100
H	-1.81838100	2.17799900	3.15169500	H	-3.38731200	2.72923500	3.77371100
O	-1.71481200	1.48858100	0.66526500	Na	-0.39627000	3.19372900	0.20684400
N	1.59133100	1.93211600	-0.27569300	Si	2.69845400	2.01640800	1.02471400

C	3.98504700	3.43065200	0.93612700	H	4.60199600	3.46476700	1.84417600
H	4.66605300	3.31085400	0.08403900	H	3.50230500	4.41061000	0.82709800
C	1.76074900	2.30059100	2.66768400	H	2.41933900	2.16881600	3.53628000
H	1.36115300	3.32203600	2.72231600	H	0.91281000	1.61442200	2.78512100
C	3.73034200	0.42909800	1.29287500	H	3.08446200	-0.44059800	1.47068800
H	4.34689400	0.20203300	0.41428000	H	4.40257400	0.52358000	2.15628300
Si	1.99700500	2.19344200	-1.91703200	C	3.60038000	1.36409200	-2.54442500
H	3.76078700	1.56837500	-3.61148600	H	4.48324700	1.73057800	-2.00539500
H	3.57309600	0.27476600	-2.41819300	C	0.59463200	1.54863600	-3.04274200
H	0.52774200	0.45356200	-3.01677100	H	-0.38742600	1.92987300	-2.73290700
H	0.74831000	1.84101400	-4.08992700	C	2.21747400	4.04765400	-2.35325400
H	1.35183200	4.64216800	-2.03012600	H	3.10031300	4.46341400	-1.85161100
H	2.34320900	4.20641700	-3.43294200	N	-1.86692800	4.74867800	-1.29340400
C	-1.65793200	4.78031900	-2.74557100	H	-1.70213900	3.76411100	-3.14576400
H	-2.42043900	5.39222100	-3.26233400	H	-0.67063000	5.19110200	-2.97303200
C	-3.16946000	4.13820000	-1.00244800	H	-4.00527800	4.72427200	-1.42993700
H	-3.19207500	3.12875000	-1.41962700	H	-3.32469200	4.04026000	0.07421100
C	-1.76705900	6.11086500	-0.74963300	H	-2.61091600	6.73752500	-1.09966000
H	-0.85795600	6.56388200	-1.15939100	C	-1.74225700	6.18980900	0.77848100
N	-0.61557700	5.49215300	1.41976500	C	0.65822100	6.17837900	1.16654200
H	0.64436700	7.22469400	1.52459400	H	1.46480700	5.64826300	1.68020800
H	0.89240500	6.17997900	0.09888900	C	-0.85454300	5.40966200	2.86677600
H	-0.02479800	4.88600800	3.34857100	H	-0.95060300	6.40827800	3.33135700
H	-1.77081800	4.84443700	3.06044600	H	-1.74645900	7.26126900	1.05780800
H	-2.66564100	5.76337100	1.18329600	H	-5.47763600	-0.28782700	0.74381200
C	-5.86623900	1.68923300	-0.03788700	H	-5.54419600	2.21096600	0.86891900
H	-5.54317000	2.29541000	-0.89248700	C	-7.37187800	1.52499800	-0.05444500
C	-8.05272100	1.07149200	1.08584300	C	-9.43565600	0.89226600	1.07118800
C	-10.1668210	1.16719900	-0.08677400	C	-9.50422700	1.62460200	-1.22609600
C	-8.11910700	1.80086200	-1.20738700	H	-7.61205000	2.16692200	-2.09770700
H	-10.0642750	1.84842000	-2.13031300	H	-11.2448180	1.03101900	-0.09808200
H	-9.94392800	0.54357300	1.96642000	H	-7.49368900	0.86654000	1.99646000
H	-5.55399500	0.28959800	-2.24484100	H	-6.10951900	-1.17038200	-1.38763200
N	-0.11132300	-1.83810200	1.89965200	C	0.39688100	-1.37258000	3.19353000
H	1.44269600	-1.06612800	3.09835200	H	-0.18621600	-0.50740900	3.52213400
H	0.33082700	-2.15110000	3.97716900	C	-1.53518000	-2.17207500	2.03075000
H	-2.09047300	-1.28598400	2.35179200	H	-1.94214600	-2.48392200	1.06705700
H	-1.69882700	-2.98476800	2.76443000	C	0.66754100	-2.99481600	1.43083500
H	0.41874800	-3.89663400	2.02393700	H	1.72493800	-2.78387800	1.62078600
C	0.46874500	-3.32719700	-0.05158400	N	1.06135600	-2.35043300	-0.97736700

C	2.52101700	-2.46996600	-1.01604300	H	2.92822200	-1.72581300	-1.70522200
H	2.95588700	-2.27764400	-0.03311700	H	2.84644500	-3.47330000	-1.35286900
C	0.51780800	-2.55311800	-2.32642800	H	-0.55916200	-2.37245100	-2.31781800
H	0.98171400	-1.84053900	-3.01537300	H	0.71666400	-3.57321300	-2.70675700
H	0.88254400	-4.33860100	-0.23535500	H	-0.60060800	-3.38337900	-0.27429000

Table A.2.25. 6b with TMEDA at –78 °C.



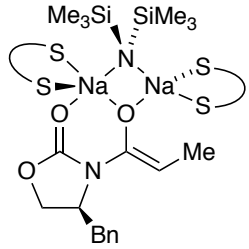


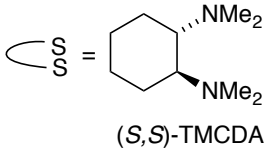
G = –2669.985141
G_{MP2} = –2669.100814

Na	0.00000000	0.00000000	0.00000000	O	1.85936200	0.12450500	-1.40781900
C	2.86876500	0.80407000	-1.30523900	O	3.83482100	0.74729900	-2.27805000
C	4.83085500	1.74667600	-1.99494100	C	4.69491800	1.97787100	-0.48608300
N	3.27312100	1.65555900	-0.31112000	C	2.43189800	2.12116100	0.80116500
C	3.06005900	2.73979900	1.84420700	H	4.13733200	2.85516800	1.84846400
C	2.31223700	3.26740400	3.03597100	H	2.71762800	2.87776800	3.98190600
H	2.35409700	4.36649600	3.11936800	H	1.25829800	2.97725600	2.98615000
O	1.16835700	1.91536100	0.65049500	Na	-0.63050800	3.11944900	0.14835200
N	-2.16392600	1.28471200	-0.10859700	Si	-2.86409300	1.28842900	-1.66961700
C	-4.20696700	-0.03169300	-2.00301500	H	-4.55727300	0.01622000	-3.04279900
H	-3.82953800	-1.04758700	-1.82989500	H	-5.08376500	0.10164000	-1.35703400
C	-3.69825500	2.95634700	-2.11466600	H	-4.08159200	2.96640800	-3.14392700
H	-4.54158700	3.16419100	-1.44385800	H	-2.99275500	3.79376200	-2.01871800
C	-1.52443800	1.00358900	-2.99916600	H	-0.66629200	1.67564100	-2.87332200
H	-1.12923800	-0.01897400	-2.95626700	H	-1.92047200	1.15736100	-4.01175300

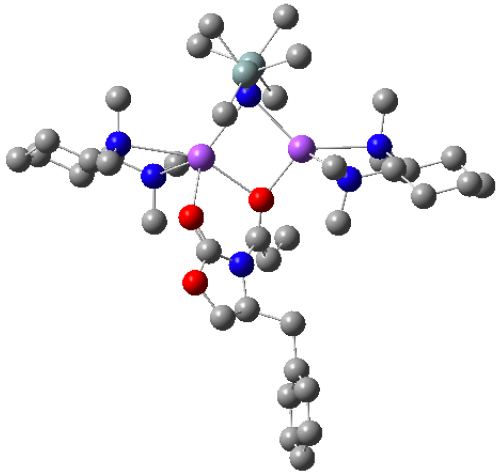
Si	-3.02499600	1.04118500	1.34839800	C	-3.35395500	-0.79718600	1.75968600
H	-3.87624300	-0.91596300	2.71850000	H	-3.96860600	-1.26995400	0.98368700
H	-2.41546400	-1.36334600	1.82101000	C	-4.73914400	1.88395900	1.47372100
H	-4.67676600	2.96527400	1.29364200	H	-5.45079500	1.47662800	0.74481300
H	-5.17597200	1.73999200	2.47115700	C	-2.01899800	1.73335900	2.82081600
H	-2.40931000	1.37748900	3.78329900	H	-0.95974800	1.45307400	2.76301200
H	-2.06282200	2.83066800	2.84611200	N	-1.20077100	5.47081000	1.14067000
C	-2.64390300	5.63478400	0.91993200	H	-2.90293500	5.44314500	-0.12421300
H	-3.18926100	4.91117100	1.53190700	H	-2.99044500	6.65073900	1.18681100
C	-0.89865600	5.64418000	2.56745600	H	0.98483200	-1.91221600	3.99365400
H	0.16339600	5.45580300	2.74761300	H	-1.14420600	6.66126900	2.92474200
H	-1.47563200	4.92629700	3.15634900	C	-0.42118900	6.44065300	0.35389400
H	0.60255100	6.43278800	0.74179100	H	-0.80503700	7.46735400	0.51082900
C	-0.40085500	6.17830700	-1.15373600	N	0.21420900	4.90162100	-1.54657400
C	-0.02266800	4.65775600	-2.97453600	H	0.41635500	3.69832800	-3.26115200
H	-1.09691400	4.61257400	-3.17384600	H	0.41961600	5.44645600	-3.61105500
C	1.65829400	4.88850000	-1.28181400	H	2.07413000	3.93764700	-1.62393600
H	2.18172800	5.71301200	-1.80205200	H	1.86440600	4.95979600	-0.21142500
H	-1.42379300	6.18609600	-1.54465700	H	0.12255300	7.02905900	-1.63272700
H	4.87141700	3.02271800	-0.21910600	C	5.61974000	1.04815300	0.34349900
H	5.27765800	1.07000200	1.38264800	H	5.48070700	0.02130900	-0.01713000
C	7.07958600	1.43691900	0.25675700	C	7.98339100	0.69819100	-0.51884000
C	9.32457700	1.07545600	-0.61557800	C	9.78486100	2.20313100	0.06442600
C	8.89633200	2.94756200	0.84405500	C	7.55831500	2.56637500	0.93862200
H	6.87724300	3.14672000	1.55794900	H	9.24742400	3.82307400	1.38410700
H	10.8283760	2.49762200	-0.00718200	H	10.0087470	0.48475300	-1.21915300
H	7.63519000	-0.18944900	-1.04300300	H	5.80560800	1.35847900	-2.29437600
H	4.60261700	2.64868400	-2.57579400	N	0.97013100	-1.56648100	1.87515600
C	0.64055000	-2.95426100	1.51902800	H	-0.39284500	-3.13997100	1.83001500
H	1.27066400	-3.66464500	2.08999400	C	0.79434400	-3.27859700	0.03001300
H	1.80162300	-3.00851500	-0.30177600	H	0.71198200	-4.37699000	-0.08963900
N	-0.16225600	-2.58794300	-0.84723500	C	-1.50113100	-3.17495700	-0.74473000
H	-2.18793800	-2.62691400	-1.39524200	H	-1.51160500	-4.24112400	-1.04299100
H	-1.88344000	-3.09817700	0.27533400	C	0.30144900	-2.65676500	-2.23864100
H	-0.43231600	-2.17452200	-2.89106100	H	1.24659100	-2.11851100	-2.33753500
H	0.43192300	-3.69995500	-2.58406300	C	2.41329300	-1.31391700	1.79075100
H	2.76378300	-1.44174300	0.76422300	H	2.61881800	-0.28122700	2.08484000
H	2.98917500	-1.99283200	2.44875100	C	0.50455500	-1.26776700	3.23312800
H	0.73130200	-0.22532400	3.47312600	H	-0.57849500	-1.40664900	3.29755300

Table A.2.26. 6a with (*S*,*S*)-TMCDA at –78 °C.





(*S*,*S*)-TMCDA



G = –2980.980268

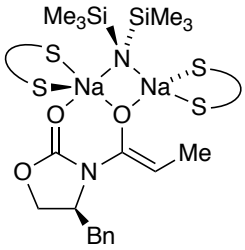
G_{MP2} = –2979.909959

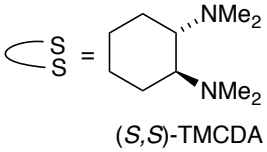
Na	0.00000000	0.00000000	0.00000000	O	0.99869200	1.69982000	-1.25352100
C	1.99820600	2.36713900	-1.04201100	O	2.33905500	3.38160900	-1.89228500
C	3.59752100	3.93729400	-1.48606400	C	3.80784200	3.44556100	-0.04265600
N	2.90234000	2.28900300	-0.01430100	C	2.67680800	1.42289700	1.16056400
C	3.00028900	1.93872700	2.38050400	H	3.33266900	2.96909300	2.45834200
C	2.86806300	1.15789300	3.65781700	H	2.08575400	1.55961900	4.32103600
H	2.60819200	0.11685800	3.44392800	H	3.79817600	1.16025200	4.24656800
O	2.19614600	0.25723600	0.88628300	Na	2.63732200	-1.86178200	0.46729200
N	0.35311400	-2.52500400	-0.03373100	Si	-0.38347700	-3.25871300	1.32791200
C	-0.22136500	-5.16334200	1.45275500	H	-0.63643300	-5.52808300	2.40216500
H	-0.75719400	-5.67816700	0.64555200	H	0.82539300	-5.49118200	1.40479600
C	0.39831200	-2.59548000	2.94449400	H	-0.26221700	-2.75362500	3.80719200
H	1.33938200	-3.11429300	3.17146400	H	0.62140200	-1.52339200	2.88571500
C	-2.26030500	-2.92861300	1.48726300	H	-2.47482100	-1.85452200	1.55839200
H	-2.80685700	-3.31554100	0.61825600	H	-2.67770700	-3.40820200	2.38281100
Si	0.32141500	-3.21005400	-1.60352400	C	-1.31735300	-4.02442700	-2.16080600
H	-1.24729700	-4.36324900	-3.20326400	H	-1.56014600	-4.90240800	-1.54928500
H	-2.17054100	-3.33851700	-2.09532500	C	0.69807200	-1.87252000	-2.91686800
H	-0.18559800	-1.25029100	-3.10962200	H	1.49895200	-1.18910200	-2.60587600
H	0.99147200	-2.31636400	-3.87725100	C	1.62446600	-4.59661900	-1.83973600
H	2.62955200	-4.26607600	-1.54673100	H	1.37520800	-5.46467200	-1.21655600
H	1.67929600	-4.94042900	-2.88160400	N	4.85367600	-1.94374000	-0.93712900
C	4.59654800	-2.15710900	-2.36575900	H	3.74786400	-1.54031700	-2.67585400

H	5.45359500	-1.89500700	-3.01036800	H	4.33519700	-3.20329300	-2.54774200
C	5.19481200	-0.53501700	-0.70510400	H	6.07327700	-0.19974000	-1.28349300
H	4.34171600	0.08778600	-0.98703500	H	5.38649600	-0.35284900	0.35512300
C	5.84192400	-2.91322000	-0.39737000	H	5.49824300	-3.89648800	-0.74820600
C	5.86259600	-2.94857600	1.15489400	N	4.50890800	-3.09085300	1.75509000
C	3.95860600	-4.45129500	1.67828400	H	4.48887600	-5.17581000	2.31820200
H	2.91235400	-4.43426300	1.99737700	H	3.98274500	-4.81528900	0.64724700
C	4.48098900	-2.60876400	3.14150300	H	3.45260800	-2.63116000	3.51344200
H	5.09870100	-3.21216100	3.82937900	H	4.82786800	-1.57169400	3.17997900
H	6.22546500	-1.97058700	1.49747800	C	6.87738400	-4.00811500	1.65180300
H	6.89307600	-4.01269000	2.74815500	H	6.54379500	-5.00669000	1.33993700
C	8.29088000	-3.77757200	1.10543800	H	8.96696300	-4.55826400	1.47578600
H	8.68334000	-2.82031800	1.47920200	C	8.27110600	-3.75828300	-0.42549200
C	7.28027300	-2.70552200	-0.93707000	H	7.26443200	-2.71079900	-2.03288400
H	7.63994000	-1.71263600	-0.63473500	H	9.27223100	-3.55350100	-0.82501300
H	7.98264700	-4.75173700	-0.79927400	H	3.45760000	4.20655500	0.66979800
C	5.27838300	3.11143900	0.26914200	H	5.31385600	2.62109600	1.24708100
H	5.63433300	2.38485100	-0.47081200	C	6.15897300	4.34375500	0.25760300
C	6.10493400	5.26736600	1.31297100	C	6.89205000	6.41839500	1.29964000
C	7.75342900	6.66724900	0.22861000	C	7.82227000	5.75509500	-0.82470300
C	7.03074000	4.60472800	-0.80799400	H	7.09740000	3.89486500	-1.62979700
H	8.49405000	5.93543800	-1.65990800	H	8.36941400	7.56237400	0.21878700
H	6.83754500	7.11886100	2.12896700	H	5.44626200	5.07664600	2.15772800
H	4.37831600	3.56093600	-2.15836800	H	3.54493800	5.02356100	-1.57450200
N	-1.48099100	1.45942000	1.62962600	C	-1.35113900	0.86737200	2.96454400
H	-1.89913300	-0.07880900	3.00895300	H	-0.29481200	0.66038000	3.16023700
H	-1.71802800	1.51955300	3.77692900	C	-0.70624800	2.70620700	1.56451900
H	0.33841300	2.48616100	1.80382500	H	-0.73636500	3.12055800	0.55400100
H	-1.05576400	3.47541200	2.27455800	C	-2.90133900	1.59652400	1.21199900
H	-3.35865800	0.61798900	1.41684200	C	-3.05043100	1.87179000	-0.30914900
N	-2.32283800	0.88435100	-1.14649800	C	-3.02683200	-0.38935400	-1.32474800
H	-2.34284400	-1.11131500	-1.77859900	H	-3.33871000	-0.79687600	-0.36024000
H	-3.91509000	-0.31391600	-1.97596700	C	-1.95986600	1.44269500	-2.45282500
H	-1.34302700	2.33375100	-2.31837500	H	-1.35829400	0.71222500	-3.00193600
H	-2.83595700	1.69499500	-3.07798400	H	-2.56774900	2.83631200	-0.51284000
C	-4.54406400	2.02430000	-0.69283000	C	-5.27232000	3.09156000	0.13112100
C	-5.15917500	2.76917000	1.62317200	C	-3.68592000	2.65492300	2.03075400
H	-3.61055600	2.41903300	3.09849000	H	-3.21559400	3.63805100	1.89600800
H	-5.65505800	3.53885100	2.22828200	H	-5.67976100	1.82289500	1.83247100
H	-6.32396900	3.14983200	-0.17719200	H	-4.83276400	4.08109200	-0.06387900

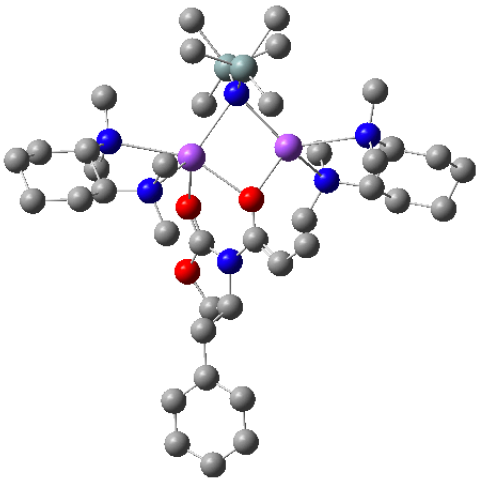
H	-4.61964700	2.25355600	-1.76268000	H	-5.05879600	1.06604600	-0.54302000

Table A.2.27. 6b with (*S*,*S*)-TMCDA at –78 °C.





(*S*,*S*)-TMCDA



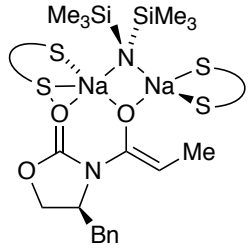
G = –2980.979634
G_{MP2} = –2979.908533

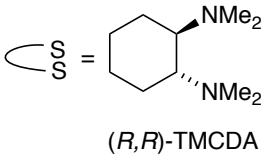
Na	0.00000000	0.00000000	0.00000000	O	0.24428000	1.71372100	-1.56017600
C	0.38268400	2.90550200	-1.33073100	O	0.89118100	3.72979200	-2.30296400
C	0.76024600	5.09346900	-1.86854700	C	0.66971300	4.99113000	-0.34101600
N	0.12662500	3.63396200	-0.19985100	C	-0.56911100	3.13394000	0.99689600
C	-0.68604900	3.99262700	2.05323100	H	-0.27853700	4.99503600	1.99861100
C	-1.31299200	3.58589500	3.35728100	H	-0.62244100	3.72154300	4.20389100
H	-2.21397800	4.16991000	3.60382700	H	-1.59779000	2.53014100	3.33097100
O	-1.00437200	1.92177700	0.91625800	Na	-3.01042800	1.04901500	0.36845800
N	-2.22953800	-1.21323000	0.04163700	Si	-2.79193900	-1.78854800	-1.47215800
C	-2.43259200	-3.62110400	-1.89099500	H	-2.77426000	-3.85819900	-2.90771800
H	-1.36414100	-3.86179300	-1.83938000	H	-2.95277400	-4.30413700	-1.20766600
C	-4.69397800	-1.64643200	-1.67083600	H	-5.02363900	-1.93921300	-2.67703400
H	-5.20261800	-2.30181200	-0.95248200	H	-5.05546400	-0.62574400	-1.49105800
C	-2.02436100	-0.77974400	-2.90341800	H	-2.01340500	0.29979400	-2.70607500
H	-0.97935400	-1.06650300	-3.08066200	H	-2.56524500	-0.94493100	-3.84476100
Si	-2.31058200	-2.13461000	1.48344700	C	-0.90227400	-3.41822400	1.65865300
H	-0.93597100	-3.93268600	2.62852500	H	-0.97577000	-4.18252900	0.87497600
H	0.08573000	-2.95062400	1.56543200	C	-3.90631400	-3.15624800	1.75647300
H	-4.80988100	-2.53589200	1.70468800	H	-4.01513800	-3.94833300	1.00504500

H	-3.89497900	-3.64176700	2.74180600	C	-2.18346400	-0.98512800	3.01119400
H	-1.83983100	-1.53072800	3.89986500	H	-1.49761600	-0.14475500	2.84356900
H	-3.16217300	-0.55534100	3.26660300	N	-5.29201400	1.65379600	1.43511800
C	-6.00054200	0.40866900	1.75159000	H	-6.29633600	-0.09619000	0.82711200
H	-5.32934100	-0.26056400	2.29723500	H	-6.89947300	0.56249700	2.37434700
C	-4.77440200	2.26699400	2.66577700	H	-4.27117300	3.21090100	2.44142000
H	-5.55308000	2.45712200	3.42339800	H	-4.03331800	1.59881700	3.11503100
C	-6.12201000	2.56446300	0.59995300	H	-6.64455500	1.90945000	-0.10953000
C	-5.26131000	3.55217200	-0.23300800	N	-4.22494700	2.85755900	-1.04311300
C	-4.74112100	2.19857600	-2.25042000	H	-3.95987700	1.55830300	-2.67032900
H	-5.59532100	1.56176800	-2.00770200	H	-5.04950100	2.90878800	-3.03582500
C	-3.12351800	3.75560500	-1.40603100	H	-2.34618700	3.17427800	-1.91071800
H	-3.42992900	4.56948400	-2.08767400	H	-2.69043600	4.19351600	-0.50196100
H	-4.70145400	4.17745000	0.47572500	C	-6.16508600	4.49124700	-1.06983100
H	-5.53930300	5.20598300	-1.61743100	H	-6.69785000	3.90017300	-1.82627400
C	-7.20663100	5.23591600	-0.22742200	H	-7.82075200	5.87599200	-0.87318100
H	-6.70315900	5.90284900	0.48790200	C	-8.07940700	4.23509200	0.53531000
C	-7.20337900	3.32665300	1.40608500	H	-7.82681100	2.60667500	1.94988000
H	-6.71507500	3.95170600	2.16502100	H	-8.81326300	4.75603800	1.16287900
H	-8.65369800	3.62986000	-0.18150300	H	-0.04066200	5.71936200	0.05789100
C	2.04173500	5.15353000	0.36134300	H	1.92881700	4.81039200	1.39453800
H	2.75755600	4.48041600	-0.12684400	C	2.55738800	6.57549400	0.32632300
C	3.59115800	6.95367900	-0.54109100	C	4.04512500	8.27366000	-0.58732200
C	3.46923400	9.24089600	0.23653000	C	2.44045300	8.87808000	1.10909100
C	1.99127900	7.55868100	1.15259000	H	1.19784200	7.28425600	1.84491600
H	1.99116600	9.62270500	1.76110400	H	3.82191000	10.2681940	0.20397500
H	4.85129700	8.54320900	-1.26465500	H	4.05414200	6.20350400	-1.17899900
H	1.62819900	5.65486700	-2.21834500	H	-0.14870700	5.51907000	-2.31039000
N	2.22609700	0.06684500	1.51072500	C	3.43643700	-0.47404100	0.84040300
C	3.13053500	-1.71331700	-0.04296800	N	2.02535400	-1.47024900	-1.00619100
C	1.43863300	-2.72344000	-1.48867800	H	0.55912900	-2.49728200	-2.09746000
H	2.12885900	-3.32247600	-2.10984200	H	1.11151300	-3.33362000	-0.64224900
C	2.39037400	-0.62240700	-2.14907900	H	1.48385300	-0.33383900	-2.68698400
H	2.86308600	0.30122800	-1.80660400	H	3.06903900	-1.12247000	-2.86124500
H	2.76332500	-2.50714400	0.62228300	C	4.42987500	-2.23244000	-0.71029400
C	5.55109800	-2.52774300	0.29304600	C	5.86591500	-1.27719300	1.11821600
C	4.59851500	-0.77730800	1.81984300	H	4.82025100	0.12044000	2.40930600
H	4.27697500	-1.54689900	2.53408800	H	6.64676400	-1.48570300	1.86057200
H	6.26351000	-0.49271800	0.45728400	H	6.44425600	-2.88012500	-0.23831100
H	5.24561400	-3.34200800	0.96661600	H	4.20450700	-3.13054300	-1.29728000

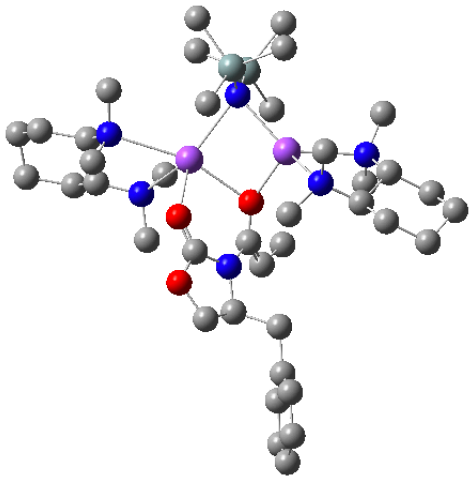
H	4.79629500	-1.48000400	-1.42118900	H	3.77622900	0.32672200	0.16989700
C	2.38217900	1.48029800	1.86372200	H	2.62462500	2.05898400	0.96702400
H	1.43927700	1.86254200	2.26261000	H	3.17074400	1.66051900	2.61724700
C	1.79546600	-0.69133100	2.69032700	H	0.80191300	-0.34672300	2.99238300
H	1.72255900	-1.75639600	2.45731200	H	2.46761900	-0.57234100	3.55760800

Table A.2.28. 6a with (*R*,*R*)-TMCDA at –78 °C.





(*R*,*R*)-TMCDA



G = –2980.979251

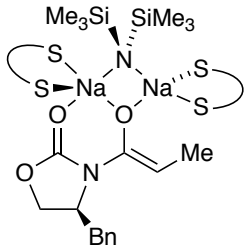
G_{MP2} = –2979.910704

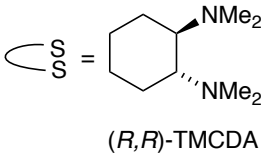
Na	0.00000000	0.00000000	0.00000000	O	1.30966000	1.37728800	-1.34241900
C	2.36201700	1.94891700	-1.10689400	O	2.85403400	2.86521600	-1.99436800
C	4.14224800	3.31484700	-1.55404500	C	4.24996400	2.86694000	-0.08371000
N	3.20078700	1.84024500	-0.02759900	C	2.83178200	1.08119800	1.18661600
C	3.20982300	1.61449100	2.38421900	H	3.69882000	2.58319800	2.41039500
C	2.92462500	0.95643200	3.70535300	H	2.26435400	1.56644900	4.34116100
H	2.43224400	-0.00780500	3.55514500	H	3.83829200	0.77999600	4.29383800
O	2.18669600	-0.01321300	0.96463800	Na	2.36165600	-2.15100800	0.39655000
N	0.00688900	-2.58303600	0.12385100	Si	-0.74218700	-3.06240400	1.58935400
C	-0.79104400	-4.94459200	1.93238800	H	-1.20508700	-5.15005500	2.92887200
H	-1.41064800	-5.48360700	1.20495900	H	0.21319500	-5.38646100	1.89395400
C	0.18059600	-2.31770500	3.09001600	H	-0.44994600	-2.30775100	3.98866200
H	1.07245900	-2.91072500	3.33606200	H	0.51812200	-1.29231300	2.89932800
C	-2.56146800	-2.49205100	1.75198800	H	-2.65371200	-1.40401000	1.63820100
H	-3.18939500	-2.95416300	0.97979800	H	-2.98734000	-2.75892500	2.72860400

Si	-0.17787000	-3.44464000	-1.34510500	C	-1.93482800	-4.05631200	-1.79009800
H	-1.93633900	-4.54432900	-2.77419500	H	-2.29579600	-4.79511000	-1.06328800
H	-2.67245800	-3.24674000	-1.82286400	C	0.39559400	-2.36305600	-2.81494600
H	-0.25917000	-1.49499400	-2.96713700	H	1.40728600	-1.96416500	-2.66140900
H	0.40563000	-2.92995800	-3.75523600	C	0.88391700	-5.04027900	-1.42256000
H	1.92965400	-4.85388000	-1.14565100	H	0.49613300	-5.79283200	-0.72468000
H	0.88267500	-5.48850600	-2.42562500	N	4.44912400	-2.37779800	-1.13020100
C	4.28701600	-3.45278000	-2.11767300	H	3.31126300	-3.34859500	-2.59940600
H	5.05529100	-3.43655400	-2.90866100	H	4.31227500	-4.43173500	-1.63249700
C	4.44548600	-1.07999700	-1.81362200	H	5.27388700	-0.96036600	-2.53447800
H	3.50774900	-0.96652800	-2.36742300	H	4.49265600	-0.27420600	-1.07754100
C	5.62959400	-2.53718100	-0.23573200	C	5.41710000	-3.65242300	0.82392600
N	4.17259500	-3.45451400	1.61757100	C	3.63901700	-4.72560100	2.12035400
H	4.30677700	-5.22622800	2.84394400	H	2.68278600	-4.54500800	2.62109400
H	3.45610600	-5.40908700	1.28523200	C	4.30274500	-2.48872000	2.71925900
H	3.31134900	-2.28432800	3.13288300	H	4.94024600	-2.84867000	3.54352100
H	4.70328500	-1.53913200	2.35386200	H	5.26685800	-4.59326900	0.27875400
C	6.68023700	-3.83263300	1.70208800	H	6.83318500	-2.93070500	2.30855200
H	6.51615400	-4.65731600	2.40638700	C	7.95473600	-4.07382200	0.88592400
H	8.81313500	-4.18502400	1.56008500	H	7.87191200	-5.01650500	0.32518000
C	8.17545600	-2.91609600	-0.09054800	C	6.95615700	-2.75924200	-1.00636700
H	6.87083400	-3.66776500	-1.61693600	H	7.11354400	-1.92984300	-1.70588400
H	9.07586300	-3.08131800	-0.69537100	H	8.34384900	-1.98776800	0.47506100
H	5.71363000	-1.58348100	0.30367100	H	3.98885500	3.69917900	0.58509900
C	5.65654700	2.35620000	0.28365100	H	5.60435100	1.90898900	1.28133800
H	5.92977300	1.55684700	-0.41579800	C	6.69501600	3.45805200	0.24459200
C	6.73402400	4.43641900	1.25012000	C	7.67035000	5.46905200	1.20971600
C	8.59050400	5.54147100	0.16122800	C	8.56732200	4.57267500	-0.84230200
C	7.62653300	3.54156900	-0.79887800	H	7.62142600	2.78539100	-1.58114200
H	9.28301600	4.61580600	-1.65917400	H	9.32249000	6.34396000	0.13050300
H	7.68574800	6.21453600	2.00050900	H	6.02961200	4.38123100	2.07742300
H	4.90850300	2.84112500	-2.17925800	H	4.19869800	4.39685800	-1.68482600
N	-1.08515100	2.13381000	1.28717600	C	-1.26615100	1.42559100	2.55854400
H	-2.03514300	0.65354900	2.46166400	H	-0.32551400	0.93364800	2.82569800
H	-1.54524300	2.08620700	3.39773700	C	-0.07617600	3.18636700	1.43694800
H	0.85444900	2.75008400	1.81207600	H	0.12786000	3.63922500	0.46112900
H	-0.38227300	3.98739400	2.13524000	C	-2.33600200	2.66502600	0.69108900
H	-2.00838400	3.40907200	-0.04625000	C	-3.15037900	1.59303800	-0.07963900
H	-3.49570700	0.84670600	0.65034100	N	-2.32137400	0.83056300	-1.04888400
C	-3.01821900	-0.36035900	-1.54148200	H	-2.32114500	-0.96595800	-2.12589400

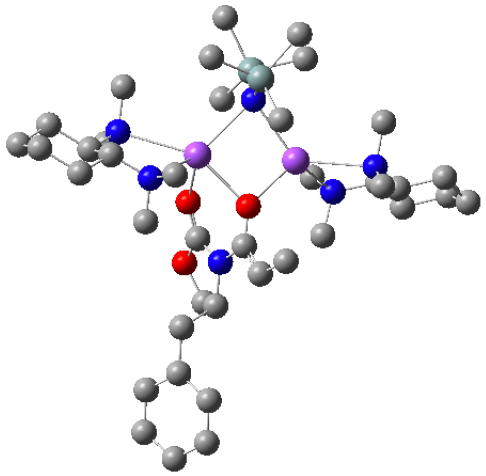
H	-3.36382000	-0.96546300	-0.69909300	H	-3.88308200	-0.13150200	-2.18918900
C	-1.82370600	1.61899800	-2.18345000	H	-1.26327100	2.48734200	-1.83333300
H	-1.12683600	1.00548300	-2.76186800	H	-2.62358900	1.95661500	-2.86489100
C	-4.40869400	2.24307700	-0.71225900	H	-4.09466500	2.96004500	-1.48311600
H	-5.00026900	1.47563700	-1.22389900	C	-5.28570100	2.98160500	0.30646800
H	-6.14706900	3.43358800	-0.20165800	H	-5.69380300	2.26535600	1.03491800
C	-4.46960800	4.04657500	1.04388700	C	-3.24281000	3.40817000	1.70400600
H	-3.59105400	2.70282100	2.47047200	H	-2.65396500	4.17150600	2.22723300
H	-5.08282200	4.55277200	1.80025100	H	-4.14849000	4.82046500	0.33093400

Table A.2.29. 6b with (*R*,*R*)-TMCDA at –78 °C.





(*R*,*R*)-TMCDA



G = –2980.981718

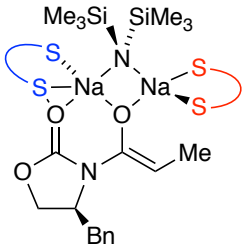
G_{MP2} = –2979.911493

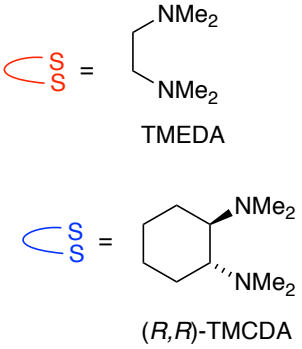
Na	0.00000000	0.00000000	0.00000000	O	0.42304000	1.75527000	-1.47830700
C	0.53297500	2.94475200	-1.22683200	O	0.97061700	3.81119500	-2.19684500
C	0.84444400	5.15690700	-1.70462800	C	0.85920000	4.99367200	-0.18032300
N	0.30952200	3.63717800	-0.06459600	C	-0.33315600	3.08918100	1.14010700
C	-0.30903300	3.85603300	2.26864100	H	0.18877000	4.81859800	2.27175100
C	-0.95113400	3.41699800	3.55445600	H	-0.22953200	3.36690200	4.38448900
H	-1.74865800	4.10161900	3.88544300	H	-1.39250800	2.42234300	3.44240200
O	-0.88185000	1.93113500	0.98464000	Na	-2.93328700	1.17533600	0.54275500
N	-2.28872700	-1.11662300	0.08488800	Si	-2.86126300	-1.63906900	-1.44378300
C	-2.63906100	-3.49511700	-1.85420900	H	-2.95202700	-3.70281700	-2.88643900

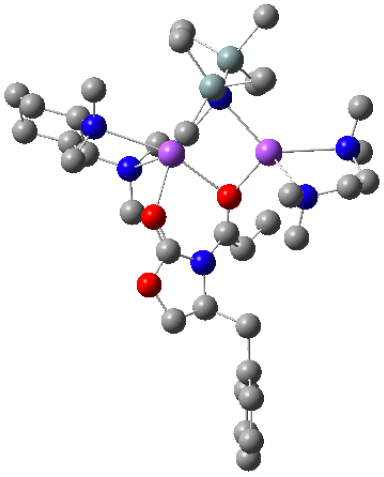
H	-1.59392100	-3.81582100	-1.75916800	H	-3.23664800	-4.13962000	-1.19803000
C	-4.73541100	-1.32087400	-1.69281400	H	-5.07127800	-1.61713100	-2.69569900
H	-5.32637300	-1.88925100	-0.96332300	H	-4.98832800	-0.25980700	-1.56151400
C	-1.97485300	-0.71432700	-2.86216600	H	-1.81656500	0.34896100	-2.64656700
H	-0.98411500	-1.14592100	-3.05563900	H	-2.54066900	-0.78580600	-3.80063200
Si	-2.39824500	-2.06356400	1.50830700	C	-1.00189000	-3.35788300	1.69474200
H	-1.09739400	-3.92504400	2.63046300	H	-1.01909100	-4.07708900	0.86662000
H	-0.01191800	-2.88396800	1.69567300	C	-4.01169300	-3.06657900	1.74693000
H	-4.90539700	-2.43250300	1.68306200	H	-4.12220800	-3.85611600	0.99362700
H	-4.02368900	-3.55247200	2.73202100	C	-2.28363600	-0.94850400	3.06028400
H	-2.00649800	-1.52880700	3.95020200	H	-1.54620800	-0.14555400	2.94100900
H	-3.25007400	-0.47590200	3.28305200	N	-5.12551300	1.98151100	1.71156300
C	-5.84964200	0.70562500	1.62175600	H	-6.07615700	0.46624600	0.57929700
H	-5.21464800	-0.09463300	2.01189500	H	-6.79050200	0.69483300	2.19682400
C	-4.84447300	2.30477900	3.11529500	H	-4.23184000	3.20957000	3.17357500
H	-5.75502100	2.45695500	3.72175500	H	-4.27631600	1.48742600	3.56923900
C	-5.79803500	3.11081200	1.01407000	H	-5.31925800	4.01743100	1.40608400
C	-5.56665600	3.09865500	-0.52159300	N	-4.13139900	2.96211600	-0.88160900
C	-3.94274000	2.64317200	-2.30170400	H	-2.89180000	2.39319600	-2.47698300
H	-4.54667500	1.77247200	-2.57315300	H	-4.20510600	3.47421700	-2.97891700
C	-3.30201000	4.11854100	-0.52013500	H	-2.25883700	3.88122200	-0.74087400
H	-3.56579800	5.03671800	-1.07234500	H	-3.36566700	4.32325400	0.55129200
H	-6.05095600	2.19778800	-0.92419000	C	-6.25796700	4.32583600	-1.16986700
H	-5.76725100	5.24454400	-0.82116700	H	-6.11907100	4.29184100	-2.25633300
C	-7.75172600	4.41907800	-0.83812000	C	-7.96168000	4.45108400	0.67846200
C	-7.30985700	3.22570300	1.32946300	H	-7.82724000	2.32752100	0.96790000
H	-7.45392900	3.25333900	2.41632900	H	-9.03085000	4.47934700	0.92310900
H	-7.52151400	5.37115800	1.09041800	H	-8.18375300	5.31053400	-1.30982200
H	-8.28168200	3.55331700	-1.26176000	H	0.18789300	5.70703200	0.30402900
C	2.28384000	5.10805800	0.42219500	H	2.24648400	4.72942300	1.44829200
H	2.94702700	4.44080900	-0.14223800	C	2.82307400	6.52163500	0.39696300
C	3.80103900	6.91016300	-0.52868900	C	4.27787100	8.22238700	-0.56368600
C	3.78100200	9.17137200	0.32995100	C	2.80808100	8.79814700	1.26027300
C	2.33600900	7.48640600	1.29242300	H	1.58676900	7.20353000	2.02917300
H	2.42068400	9.52846100	1.96597100	H	4.15170600	10.1925550	0.30622300
H	5.04005200	8.50009400	-1.28708400	H	4.20184200	6.17359100	-1.22203700
H	1.67691400	5.74687300	-2.09136200	H	-0.10072600	5.57891400	-2.06693900
N	2.08921900	-0.25274500	1.58299700	C	3.01831000	-1.33931800	1.17891400
H	2.49512500	-2.27318000	1.42907200	C	3.28782200	-1.35040100	-0.35030200
H	3.78925100	-0.40536300	-0.59679500	N	2.03857500	-1.35282400	-1.15414400

C	1.40615900	-2.67075800	-1.27876700	H	0.41208600	-2.54909800	-1.71754000
H	1.97112500	-3.36992300	-1.91943300	H	1.27551400	-3.13001700	-0.29591000
C	2.24539000	-0.76858000	-2.48328100	H	1.28474600	-0.69491700	-3.00036900
H	2.63882500	0.24645000	-2.38675700	H	2.93025700	-1.36053900	-3.11778600
C	4.26825800	-2.49073700	-0.72390200	H	3.79249900	-3.46018800	-0.52588900
H	4.46748700	-2.45639400	-1.80192300	C	5.58252400	-2.43421400	0.06191600
H	6.23306900	-3.26618200	-0.23631200	H	6.12575600	-1.50883200	-0.18097700
C	5.29746000	-2.47811400	1.56523800	H	6.22921800	-2.41172200	2.14125300
H	4.83962700	-3.44497100	1.82176100	C	4.35705700	-1.33424200	1.96212100
H	4.87870900	-0.38431800	1.78386800	H	4.15027800	-1.37723100	3.03760500
C	2.62760500	1.10338500	1.42575800	H	2.89438300	1.29106200	0.38196100
H	1.85283000	1.82070000	1.70824400	H	3.51127700	1.30231500	2.05620700
C	1.58315600	-0.42702400	2.94821500	H	0.78533000	0.30068200	3.12341400
H	1.16315500	-1.43054500	3.06500400	H	2.35084900	-0.27948400	3.72822100

Table A.2.30. 6a with TMEDA and (*R*,*R*)-TMCDA at –78 °C.







G = –2825.480621

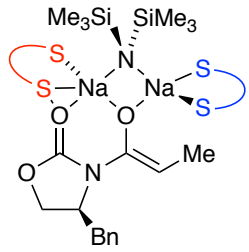
G_{MP2} = –2824.50266

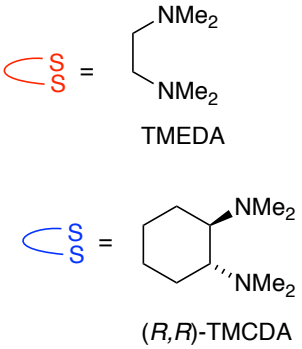
Na	0.00000000	0.00000000	0.00000000	O	-1.70657400	-0.93229300	-1.25519600
C	-2.89506700	-1.05738800	-1.01213700	O	-3.68616200	-1.80254900	-1.84144700
C	-5.05015800	-1.71204400	-1.41175700	C	-4.99083800	-1.13619700	0.01590600
N	-3.63896800	-0.56056200	0.02906700	C	-3.02060900	0.09423600	1.19892600
C	-3.58373500	-0.14604900	2.41838800	H	-4.41092100	-0.84248600	2.50715300
C	-3.07724200	0.48592800	3.68488200	H	-2.76932600	-0.26240900	4.43084500

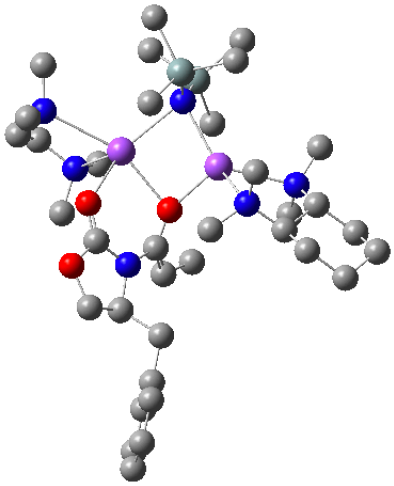
H	-2.20726200	1.11587800	3.47578500	H	-3.83668000	1.11338500	4.17926200
O	-2.00271500	0.83859400	0.92900200	Na	-1.29530000	2.90396900	0.65182400
N	0.97546800	2.37355300	0.03867400	Si	2.03248300	2.65857600	1.35416200
C	2.79391300	4.41269600	1.45580800	H	3.40450700	4.52480300	2.36189200
H	3.44176600	4.63117200	0.59780100	H	2.02005000	5.19105500	1.48184400
C	1.10620400	2.43799900	3.01289600	H	1.79882400	2.45198800	3.86467700
H	0.38595800	3.25153300	3.17302100	H	0.54478500	1.49721800	3.05513900
C	3.53377600	1.47749300	1.43670800	H	3.21940700	0.42676700	1.48463000
H	4.16955200	1.58849800	0.54913200	H	4.15877300	1.67479800	2.31800200
Si	1.21621200	3.00137400	-1.53615400	C	2.99783600	2.96037500	-2.22984600
H	3.02362300	3.34800400	-3.25726400	H	3.67719300	3.58116900	-1.63220300
H	3.41739600	1.94803500	-2.24986800	C	0.13485600	2.05241100	-2.79506200
H	0.50709000	1.03378100	-2.96750100	H	-0.90365600	1.95012600	-2.45346500
H	0.11610000	2.55619500	-3.77050700	C	0.71042200	4.84585900	-1.68813200
H	-0.30756500	5.02003300	-1.31464400	H	1.38471100	5.47995400	-1.09874400
H	0.74581900	5.20039800	-2.72729300	N	-3.23868300	4.05210300	-0.68511400
C	-3.10703100	4.25885800	-2.13202900	H	-2.85347000	3.31189200	-2.61645200
H	-4.04048100	4.64283300	-2.58394900	H	-2.30361900	4.97068300	-2.33824400
C	-4.29294500	3.06363300	-0.43199700	H	-5.28185700	3.41505400	-0.78367600
H	-4.04258900	2.13412500	-0.94795200	H	-4.36290600	2.82709300	0.63193600
C	-3.51883400	5.33396700	-0.02207600	H	-4.51580200	5.71868000	-0.31446900
H	-2.78776700	6.06241000	-0.38914800	C	-3.47873700	5.28349700	1.50735200
N	-2.17978100	4.89656900	2.08237700	C	-1.18375500	5.96418300	1.92171000
H	-1.50628100	6.90722700	2.40108200	H	-0.23894200	5.65195800	2.37472300
H	-0.99387100	6.15994200	0.86342800	C	-2.34923800	4.58747400	3.50847200
H	-1.38694500	4.30168000	3.94152100	H	-2.74264000	5.44918900	4.07845700
H	-3.03840700	3.74606000	3.62661800	H	-3.79135000	6.27667700	1.88388500
H	-4.22517200	4.56974200	1.87012500	H	-5.05384400	-1.94752700	0.75487800
C	-6.11846100	-0.12275800	0.29171700	H	-5.91937600	0.35478400	1.25598300
H	-6.07446800	0.66113400	-0.47332900	C	-7.48608100	-0.77397800	0.29150400
C	-7.88381100	-1.59685300	1.35669900	C	-9.13116300	-2.22031700	1.35446700
C	-10.0089740	-2.03000900	0.28469300	C	-9.62967700	-1.21025300	-0.77840200
C	-8.37876800	-0.58938700	-0.77278500	H	-8.09593000	0.05564200	-1.60202100
H	-10.3075420	-1.04969200	-1.61271900	H	-10.9823550	-2.51300100	0.28332500
H	-9.42074500	-2.85058900	2.19129300	H	-7.21231100	-1.74196900	2.20038900
H	-5.58727100	-1.04384600	-2.09567100	H	-5.49998300	-2.70510100	-1.46205100
N	0.29117800	-2.26662000	1.49173600	C	0.70060800	-1.51652900	2.68203000
H	1.66999600	-1.03532800	2.51957500	H	-0.03944800	-0.73241100	2.87198900
H	0.77207400	-2.13350000	3.59505800	C	-1.00636800	-2.90761800	1.72063900
H	-1.73884200	-2.15270400	2.02319500	H	-1.35706600	-3.36854700	0.79132700

H	-0.97606800	-3.68652900	2.50533300	C	1.29647700	-3.23287900	0.98481500
H	0.73475300	-3.91760600	0.33681200	C	2.38769300	-2.57152400	0.10134000
H	2.97210100	-1.89542000	0.74179300	N	1.81760900	-1.70272700	-0.96121400
C	2.84767700	-0.88741500	-1.61072800	H	2.36490800	-0.15539100	-2.26354500
H	3.42018600	-0.34018100	-0.85760000	H	3.54858200	-1.47280000	-2.23175600
C	1.03686300	-2.41417500	-1.98084800	H	0.22850300	-2.98499900	-1.52113000
H	0.56680600	-1.68042500	-2.64119000	H	1.64699900	-3.09146800	-2.60339900
C	3.35765700	-3.65667100	-0.43462600	H	2.81286300	-4.32218500	-1.11807100
H	4.14835500	-3.18275500	-1.02668800	C	3.98477100	-4.50518300	0.67788200
H	4.64850800	-5.26248700	0.24166800	H	4.61433700	-3.86907700	1.31761000
C	2.89721600	-5.16319600	1.53130900	H	2.33264900	-5.87956800	0.91644300
H	3.34215400	-5.73894200	2.35290100	C	1.94694100	-4.09874300	2.09220800
H	2.51472700	-3.45319800	2.77544200	H	1.15966100	-4.57174800	2.69230000

Table A.2.31. 6a with (*R*,*R*)-TMCDA and TMEDA at –78 °C.







G = –2825.482535

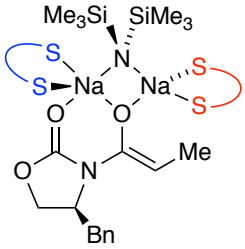
G_{MP2} = –2824.505237

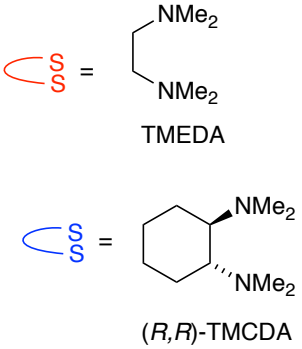
Na	0.00000000	0.00000000	0.00000000	O	-1.73894900	-0.98833900	-1.21645000
C	-2.94850800	-0.95366300	-1.04547500	O	-3.77849200	-1.64788800	-1.88014100
C	-5.14153900	-1.36547900	-1.53081800	C	-5.07612800	-0.75800300	-0.11820200
N	-3.67629000	-0.31356400	-0.07971300	C	-3.03195700	0.35971600	1.06977200
C	-3.59897800	0.15500500	2.29310200	H	-4.44623500	-0.51799500	2.38431600
C	-3.08373800	0.78666600	3.55595600	H	-2.82250100	0.03618500	4.31749900
H	-2.18362200	1.37217400	3.35014000	H	-3.81909500	1.45708500	4.02882100

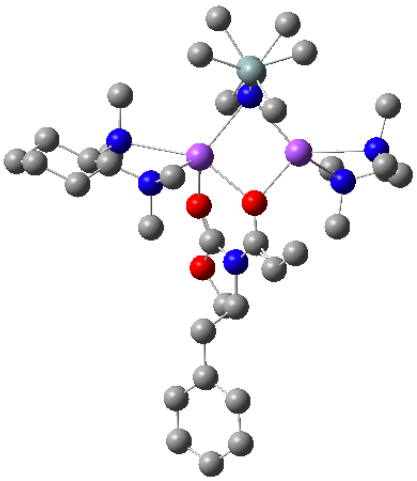
O	-1.99931200	1.06921400	0.76625900	Na	-1.11051100	3.01396500	0.18890300
N	1.14980100	2.25265500	-0.07747800	Si	2.09812400	2.40255600	1.34074900
C	3.07967900	4.03402400	1.52991900	H	3.58757700	4.07585000	2.50293600
H	3.85013600	4.14159900	0.75586500	H	2.42569600	4.91301700	1.46048900
C	0.99577100	2.29613800	2.90045700	H	1.59240200	2.08206800	3.79698500
H	0.47166400	3.24300300	3.08886000	H	0.23122700	1.51483600	2.81105600
C	3.40272600	1.01867500	1.54579400	H	2.92983700	0.02818700	1.57017000
H	4.11414900	1.01746500	0.71107000	H	3.97735300	1.13404600	2.47472300
Si	1.68060100	2.74633900	-1.62812700	C	3.47058800	2.28592900	-2.11706200
H	3.69101500	2.60761300	-3.14382700	H	4.20709900	2.76678700	-1.46093400
H	3.64808500	1.20501200	-2.06534300	C	0.56603100	1.96893300	-2.97276200
H	0.69649800	0.88005400	-3.01510600	H	-0.50199700	2.14611600	-2.78685600
H	0.79582700	2.36498500	-3.97080200	C	1.60260500	4.64319000	-1.89213200
H	0.61416100	5.05457100	-1.64951700	H	2.32955300	5.15021000	-1.24546500
H	1.83062600	4.92278200	-2.92977900	N	-2.87393300	4.16146200	-1.31875900
C	-2.21706300	4.88376500	-2.41590900	H	-1.45966000	4.23651100	-2.86584200
H	-2.91205700	5.19158800	-3.21505400	H	-1.70818500	5.77550100	-2.04088600
C	-3.58860700	2.99592000	-1.84919200	H	-4.40993400	3.26102700	-2.53889500
H	-2.88574200	2.36236000	-2.40017200	H	-3.98955400	2.40152000	-1.02500200
C	-3.74482500	5.00859400	-0.45844500	H	-4.31400100	4.30155200	0.16074700
C	-2.92126000	5.90941300	0.50231000	N	-1.94411600	5.13603600	1.31564700
C	-0.80556600	5.96359600	1.73070200	H	-1.08573800	6.78523600	2.41365200
H	-0.07088300	5.33840300	2.24682300	H	-0.31842900	6.39377400	0.85003600
C	-2.53034500	4.45706600	2.48056400	H	-1.78455400	3.78550800	2.91544600
H	-2.85729200	5.14909600	3.27404400	H	-3.38366200	3.84406700	2.17766500
H	-2.31393000	6.57795100	-0.12212100	C	-3.85482000	6.80346300	1.35521800
C	-4.82489700	7.63668000	0.51138200	C	-5.67134100	6.71875200	-0.37520700
C	-4.76406400	5.85587100	-1.26071900	H	-4.21975000	6.52382000	-1.94103300
H	-5.36964000	5.19524700	-1.89258700	H	-6.35456300	7.30424900	-1.00310400
H	-6.30105200	6.07662500	0.25804600	H	-4.26381200	8.34074700	-0.12076300
H	-5.46288400	8.24343400	1.16593800	H	-4.44678200	6.17134700	2.03010100
H	-3.24775200	7.45704300	1.99341800	H	-5.23658600	-1.54148400	0.63671600
C	-6.10574300	0.36420200	0.10560200	H	-5.87355800	0.84782300	1.06002200
H	-5.97645900	1.11798600	-0.68023000	C	-7.52836100	-0.15555600	0.10097400
C	-8.03175100	-0.86148400	1.20441100	C	-9.33029200	-1.37001400	1.19856900
C	-10.1537100	-1.17899900	0.08657700	C	-9.66878700	-0.47399100	-1.01529900
C	-8.36733700	0.03210100	-1.00565700	H	-8.00109800	0.58837500	-1.86607300
H	-10.3034040	-0.31370600	-1.88301500	H	-11.1666630	-1.57225700	0.08217700
H	-9.70180800	-1.91071700	2.06514900	H	-7.40192600	-1.00472600	2.07993500
H	-5.54698100	-0.65213200	-2.25872200	H	-5.71459200	-2.29250000	-1.58290000

N	1.52409100	-1.99490000	-1.14934000	C	1.15707000	-3.16486900	-0.33793200
C	1.23738500	-2.93553700	1.17450400	N	0.20645900	-2.02818100	1.70144500
C	0.54629400	-1.61135700	3.06588600	H	1.50749900	-1.08931600	3.07091300
H	-0.21938500	-0.92464900	3.43751200	H	0.61082000	-2.46852100	3.76271300
C	-1.11491000	-2.66897400	1.70742600	H	-1.85968200	-1.96275400	2.08554900
H	-1.40801500	-2.94658300	0.69292900	H	-1.12645200	-3.57774800	2.33956800
H	1.18104000	-3.92158800	1.67646100	H	2.21536700	-2.51487100	1.43080100
H	1.80137900	-4.03040500	-0.58913500	H	0.13708000	-3.44975200	-0.61144000
C	2.97474900	-1.78929000	-1.15573500	H	3.21513100	-0.91370600	-1.76378600
H	3.51579600	-2.66161900	-1.57084400	H	3.34688700	-1.60014400	-0.14650900
C	1.04578900	-2.17506500	-2.52577200	H	-0.04498000	-2.22900900	-2.52937600
H	1.34858500	-1.31503200	-3.13075800	H	1.46124300	-3.08613200	-2.99702800

Table A.2.32. 6b with TMEDA and (*R*,*R*)-TMCDA at –78 °C.







G = –2825.483369

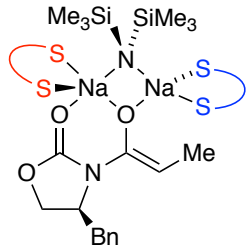
G_{MP2} = –2824.505837

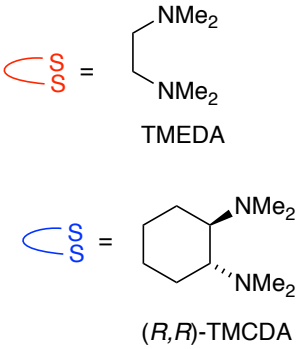
Na	0.00000000	0.00000000	0.00000000	O	-1.67123700	-0.63969300	-1.49333100
C	-2.69791800	-1.25965400	-1.26822200	O	-3.66457400	-1.35407800	-2.23841900
C	-4.67839600	-2.27110400	-1.79343100	C	-4.54265200	-2.25781100	-0.26668200
N	-3.12081400	-1.91366200	-0.13932000	C	-2.30392500	-2.15906700	1.05814300
C	-2.93329900	-2.68094000	2.15212600	H	-3.99650200	-2.88873800	2.13268800
C	-2.20406000	-2.97231900	3.43337300	H	-2.66415300	-2.46643200	4.29580500
H	-2.19083900	-4.04610500	3.68368000	H	-1.16568600	-2.63341700	3.36785000
O	-1.05271600	-1.86816400	0.93728300	Na	0.78542300	-3.04900900	0.50647000

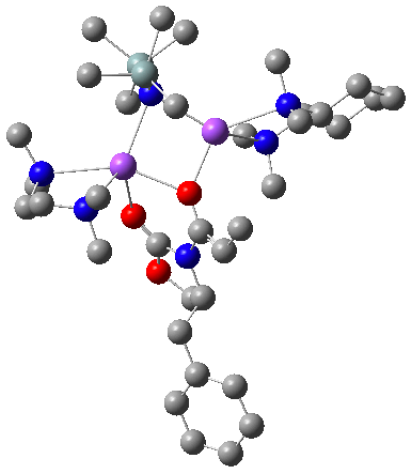
N	2.24944100	-1.19252600	0.03761400	Si	2.97276600	-1.35964900	-1.50640200
C	4.34011600	-0.09765200	-1.95153200	H	4.68051900	-0.24083200	-2.98595800
H	3.99083300	0.93863800	-1.86220400	H	5.21909700	-0.19939400	-1.30301300
C	3.80721700	-3.06667500	-1.76667000	H	4.19137900	-3.18539800	-2.78886700
H	4.65168200	-3.19728900	-1.07832800	H	3.10640600	-3.89215800	-1.58116000
C	1.66418400	-1.19589500	-2.88811500	H	0.73318100	-1.72604700	-2.65304000
H	1.39223300	-0.14527700	-3.05479400	H	2.03972700	-1.58272900	-3.84469000
Si	3.11416700	-0.79548600	1.46074700	C	3.37200800	1.08156500	1.72227300
H	3.90718700	1.29220800	2.65791600	H	3.95321500	1.51927700	0.90104700
H	2.41277300	1.61376500	1.76462000	C	4.86280000	-1.55416200	1.64177500
H	4.84758000	-2.64832300	1.55256800	H	5.55884500	-1.17780400	0.88230900
H	5.29100200	-1.31078200	2.62363700	C	2.15863600	-1.40678900	3.00071100
H	2.55930000	-0.97047800	3.92519200	H	1.09076400	-1.16278600	2.94934800
H	2.23760300	-2.49740500	3.10338600	N	1.43947500	-5.27170100	1.72450700
C	2.89498400	-5.37445900	1.55347400	H	3.17093200	-5.27633100	0.50081400
H	3.38326900	-4.56219000	2.09858000	H	3.28944300	-6.33627000	1.93136300
C	1.10660800	-5.32680700	3.15400700	H	0.03098000	-5.18418100	3.29122200
H	1.39806500	-6.28958500	3.61274800	H	1.62552000	-4.52417400	3.68454400
C	0.73710800	-6.35319100	1.01395000	H	-0.29154900	-6.38057000	1.38720200
H	1.18313800	-7.33580200	1.26122400	C	0.72427800	-6.21736600	-0.51044600
N	0.02763400	-5.02300600	-1.01120200	C	0.25342000	-4.88504000	-2.45546800
H	-0.23168900	-3.97450300	-2.81779300	H	1.32395500	-4.80348200	-2.66086300
H	-0.14799600	-5.74455200	-3.02374700	C	-1.41542000	-5.08645200	-0.74827500
H	-1.89583800	-4.21141900	-1.19165100	H	-1.87425200	-5.99729600	-1.17753500
H	-1.62559700	-5.05685000	0.32342300	H	1.75152000	-6.18472100	-0.88884100
H	0.26857500	-7.13885000	-0.92338200	H	-4.72416500	-3.24899400	0.15621600
C	-5.46620000	-1.21227100	0.41106700	H	-5.12220800	-1.07953100	1.44157100
H	-5.32769700	-0.25196000	-0.10103900	C	-6.92581000	-1.61037600	0.38596400
C	-7.83103600	-1.00167400	-0.49398200	C	-9.17170300	-1.39136500	-0.53047200
C	-9.63027000	-2.40087200	0.31608100	C	-8.74065700	-3.01393300	1.20152300
C	-7.40323300	-2.62075500	1.23516100	H	-6.72151800	-3.09646700	1.93737300
H	-9.09035500	-3.79544600	1.87114400	H	-10.6733490	-2.70446500	0.29119100
H	-9.85692900	-0.90219600	-1.21787700	H	-7.48460500	-0.20520300	-1.14943800
H	-5.64721000	-1.91825900	-2.15060100	H	-4.47206500	-3.26076400	-2.21876800
N	-1.01049500	1.77823100	1.64288000	C	-0.66973200	3.18064000	1.29071700
H	0.39163000	3.29306400	1.55415900	C	-0.80698900	3.46131200	-0.23013300
H	-1.86688600	3.33742700	-0.48750500	N	-0.08144300	2.47040600	-1.06575500
C	1.36032100	2.71920900	-1.17778700	H	1.83716100	1.84952000	-1.63805300
H	1.60634200	3.60124600	-1.79396700	H	1.80661500	2.85232700	-0.18925700
C	-0.67404000	2.34679100	-2.40151100	H	-0.17006600	1.54529900	-2.94879700

H	-1.72751300	2.06825800	-2.31750300	H	-0.59231300	3.27180300	-3.00103000
C	-0.43645100	4.93205000	-0.54749000	H	0.62789100	5.09410800	-0.33294500
H	-0.56932700	5.11463700	-1.62078000	C	-1.24980000	5.94361400	0.26782000
H	-0.94122500	6.96525700	0.01235000	H	-2.31574000	5.86360500	0.00748800
C	-1.07008600	5.67925800	1.76508200	H	-1.67066200	6.37921700	2.35978100
H	-0.02008900	5.85355000	2.04285500	C	-1.46353800	4.23632800	2.10316800
H	-2.53664900	4.11562800	1.90324300	H	-1.32446100	4.05291300	3.17474800
C	-2.42679800	1.43072800	1.47646600	H	-2.74259700	1.59246200	0.44220100
H	-2.55253000	0.36938800	1.70490500	H	-3.10057400	1.99724900	2.14194400
C	-0.57204800	1.42013800	2.99536300	H	-0.70655900	0.34338300	3.13441200
H	0.49036000	1.65201800	3.11772300	H	-1.13371600	1.93567300	3.79436600

Table A.2.33. 6b with (*R*,*R*)-TMCDA and TMEDA at –78 °C.







G = –2825.483544

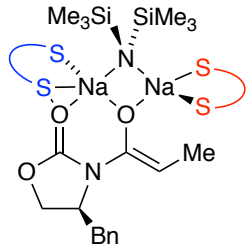
G_{MP2} = –2824.506824

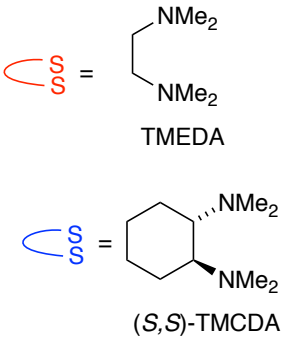
Na	0.00000000	0.00000000	0.00000000	O	1.64778700	0.80309600	-1.45045100
C	2.48876600	1.66564200	-1.24889800	O	3.40746400	1.96797300	-2.22218200
C	4.16492700	3.11561000	-1.79718300	C	4.03683800	3.09121100	-0.27004900
N	2.73244200	2.43003900	-0.13855400	C	1.83994700	2.54119500	1.02585200
C	2.34565900	3.13328200	2.14678200	H	3.37211600	3.47990900	2.16920000
C	1.53053400	3.33314700	3.39328300	H	2.02519300	2.91061300	4.28094200
H	1.35127300	4.39650900	3.62268300	H	0.55549200	2.84644900	3.29726300
O	0.64876200	2.08299300	0.84010300	Na	-1.39755000	2.84033900	0.41935700
N	-2.43167400	0.67465400	0.07999700	Si	-3.21648200	0.56194900	-1.43840400

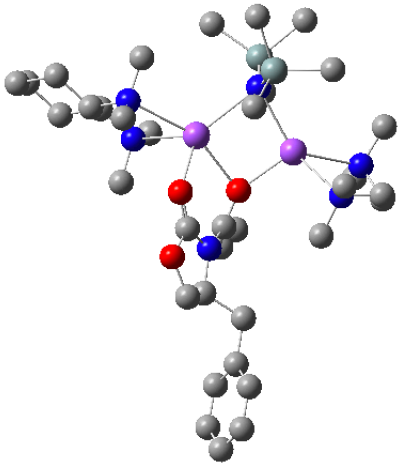
C	-4.27075900	-1.00602500	-1.74217200	H	-4.66826700	-1.01412500	-2.76605900
H	-3.68427000	-1.92439900	-1.61082200	H	-5.12805700	-1.06943600	-1.06061600
C	-4.41611500	2.01925900	-1.77117100	H	-4.86209300	1.96593400	-2.77345600
H	-5.23658600	2.02125400	-1.04197700	H	-3.90552100	2.98872500	-1.68965900
C	-1.94544600	0.57802500	-2.86300300	H	-1.17678100	1.35093400	-2.74156400
H	-1.41801100	-0.38242700	-2.92020100	H	-2.42939700	0.73892600	-3.83542800
Si	-3.11004800	0.09792400	1.54217000	C	-2.93454100	-1.79180100	1.79012000
H	-3.32450500	-2.11425800	2.76502200	H	-3.48215400	-2.34223400	1.01504900
H	-1.88490800	-2.10782200	1.73282800	C	-4.97429600	0.44126300	1.81078400
H	-5.21392800	1.50959400	1.73300800	H	-5.59580700	-0.08183200	1.07374400
H	-5.29484800	0.10389100	2.80571100	C	-2.23222600	0.90360500	3.03931200
H	-2.43747600	0.35625800	3.96859900	H	-1.14443100	0.94344700	2.90450000
H	-2.57897400	1.93400500	3.19892400	N	-2.48576300	4.94509300	1.49083600
C	-3.87395400	4.46670700	1.41953300	H	-4.19759600	4.38109900	0.37868900
H	-3.93193200	3.46907400	1.86417400	H	-4.58795800	5.11285400	1.95674400
C	-2.06923500	5.07232200	2.89236400	H	-1.01307800	5.35366800	2.94325400
H	-2.65861200	5.81424600	3.45962700	H	-2.18191500	4.10649800	3.39383500
C	-2.23565900	6.19995900	0.73105600	H	-1.27066200	6.57122700	1.09968800
C	-2.08325700	5.96567700	-0.79623500	N	-1.11333800	4.88569500	-1.11558100
C	-1.19776500	4.46095800	-2.51752000	H	-0.59026300	3.56148500	-2.65703600
H	-2.23229500	4.21299200	-2.77235300	H	-0.83518700	5.22051400	-3.23138800
C	0.28136800	5.19501200	-0.77616200	H	0.88871900	4.30541200	-0.96058500
H	0.70238000	6.02507900	-1.36859400	H	0.37948000	5.43569700	0.28521700
H	-3.04951500	5.60347000	-1.17516800	C	-1.77959100	7.30910700	-1.50839000
C	-2.82262800	8.39460900	-1.21607800	C	-2.94578300	8.62681700	0.29213200
C	-3.28014600	7.31066400	1.00344300	H	-4.26804100	6.97575400	0.66077800
H	-3.36344000	7.47512100	2.08441100	H	-3.71751500	9.37580400	0.50926400
H	-1.99878300	9.03076900	0.67960600	H	-2.54826100	9.32321200	-1.73208700
H	-3.79953600	8.08992300	-1.61948600	H	-0.79669500	7.67694000	-1.18411800
H	-1.70907700	7.14257600	-2.58917400	H	3.98219100	4.09971100	0.14698000
C	5.17829200	2.29091100	0.41122000	H	4.88371600	2.09528500	1.44674900
H	5.25592100	1.31712500	-0.08834700	C	6.51098700	3.00610900	0.36567400
C	7.52299900	2.60048500	-0.51494300	C	8.74323000	3.27760800	-0.56953900
C	8.97113700	4.37648500	0.25896400	C	7.97291700	4.79052800	1.14415800
C	6.75648500	4.11061200	1.19604200	H	5.98977200	4.43420000	1.89723600
H	8.14430900	5.64068600	1.79933600	H	9.92050900	4.90371600	0.22006700
H	9.51574300	2.94245200	-1.25673000	H	7.35780400	1.73700500	-1.15600000
H	5.18990100	3.00583600	-2.15465600	H	3.71885900	4.01617000	-2.23615700
N	1.39294800	-1.45403500	1.70276300	C	1.37762900	-2.84285300	1.22054600
H	0.41408000	-3.28107600	1.50159600	H	2.15515900	-3.44376600	1.73305900

C	1.59035400	-2.99022900	-0.28844400	H	2.52179700	-2.49275400	-0.57524900
H	1.73475500	-4.06626700	-0.50867000	N	0.51313400	-2.43025600	-1.11743400
C	-0.67022300	-3.29503900	-1.11075400	H	-1.45800500	-2.83734700	-1.71527100
H	-0.45309000	-4.30039200	-1.52036600	H	-1.05992800	-3.41205400	-0.09705600
C	0.99034200	-2.25168500	-2.49431500	H	0.17739100	-1.86741000	-3.11630600
H	1.79785100	-1.51652600	-2.51046600	H	1.34488200	-3.20067100	-2.93942700
C	2.73456800	-0.86500200	1.62321000	H	3.06808500	-0.80662800	0.58433500
H	2.70605700	0.15359200	2.01948400	H	3.47713400	-1.45054500	2.19883600
C	0.92121500	-1.39587000	3.08994100	H	0.91000200	-0.35548100	3.42587100
H	-0.09724100	-1.78834700	3.15636800	H	1.56534500	-1.97696700	3.77677900

Table A.2.34. 6a with TMEDA and (*S*,*S*)-TMCDA at –78 °C.







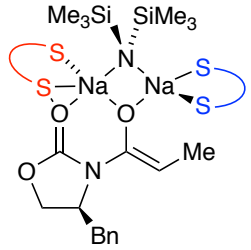
G = –2825.482008
G_{MP2} = –2824.504717

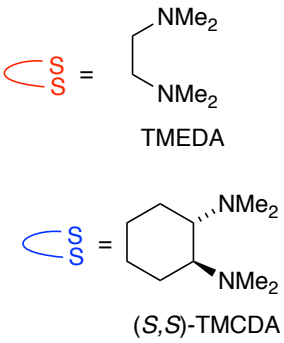
Na	0.00000000	0.00000000	0.00000000	O	-1.69597700	-1.02269000	-1.24150300
C	-2.89116300	-1.13117900	-1.02154800	O	-3.67974600	-1.86651300	-1.86213100
C	-5.04882600	-1.74990000	-1.45173700	C	-4.99519600	-1.19703800	-0.01561300
N	-3.64274500	-0.62356900	0.00655100	C	-3.02794400	0.03998300	1.17419200
C	-3.56330000	-0.23840900	2.39725800	H	-4.35655800	-0.97414400	2.48396200
C	-3.07452100	0.40204800	3.66618900	H	-2.64602900	-0.32886600	4.36940500
H	-2.29468400	1.13774100	3.44696900	H	-3.87989600	0.91594300	4.21433500
O	-2.04410200	0.82526700	0.89328400	Na	-1.35438400	2.88182800	0.54369300
N	0.94227800	2.37783400	-0.01663300	Si	1.94268200	2.68945600	1.33763500
C	2.70252800	4.44437200	1.43629100	H	3.26036000	4.57773200	2.37303800

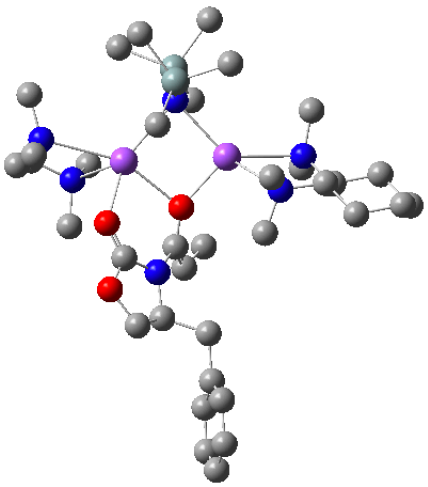
H	3.39950000	4.64069700	0.61206200	H	1.93014600	5.22379900	1.39869400
C	0.94086800	2.50489700	2.95631300	H	1.59658000	2.47726400	3.83653700
H	0.25929300	3.35513000	3.09405600	H	0.33021400	1.59426100	2.96519300
C	3.43362400	1.50552200	1.51006700	H	3.10939900	0.46156800	1.61102400
H	4.08474800	1.56284300	0.62875800	H	4.04335800	1.74756100	2.39085900
Si	1.22646300	3.00796700	-1.58286900	C	3.02767200	2.97054200	-2.22650300
H	3.08217600	3.37426900	-3.24661200	H	3.69551400	3.57653600	-1.60142100
H	3.44356200	1.95600600	-2.25432300	C	0.19866500	2.04500100	-2.87496000
H	0.62558400	1.05088200	-3.06151600	H	-0.83768300	1.88570200	-2.54922900
H	0.16862500	2.56684200	-3.84051700	C	0.71708400	4.84962400	-1.75102500
H	-0.31168600	5.01882600	-1.40575300	H	1.37120100	5.48752000	-1.14351700
H	0.77971400	5.20386100	-2.78895400	N	-3.25433500	3.97367200	-0.88821900
C	-3.06890900	4.15178200	-2.33308000	H	-2.79486000	3.19638500	-2.78868800
H	-3.98571300	4.52369100	-2.82721000	H	-2.26001900	4.86196900	-2.52287400
C	-4.30925300	2.98153600	-0.65381100	H	-5.28708500	3.31549200	-1.05066600
H	-4.03131700	2.04276300	-1.13816000	H	-4.41712500	2.76909700	0.41193500
C	-3.56881900	5.26714800	-0.26420000	H	-4.55349700	5.64125900	-0.60783500
H	-2.82489600	5.99115900	-0.61378100	C	-3.59535700	5.24789900	1.26617400
N	-2.31990400	4.88127100	1.90379200	C	-1.33106500	5.96073700	1.78275500
H	-1.68345800	6.89940200	2.24950700	H	-0.40060700	5.65988500	2.27199100
H	-1.10278800	6.16005100	0.73272500	C	-2.54964000	4.57545200	3.32202500
H	-1.60486400	4.29965300	3.79784800	H	-2.97592800	5.43498200	3.87132300
H	-3.23524600	3.72767600	3.41245900	H	-3.93055400	6.24570800	1.60918800
H	-4.35230100	4.53612800	1.61032900	H	-5.06002500	-2.02146200	0.70901700
C	-6.11962600	-0.18682900	0.27905200	H	-5.91682900	0.27029400	1.25269000
H	-6.07364200	0.61201900	-0.47024900	C	-7.48937600	-0.83324100	0.26790900
C	-7.89332000	-1.66514900	1.32361900	C	-9.14298700	-2.28389700	1.31129300
C	-10.0167250	-2.07962000	0.24078200	C	-9.63108200	-1.25080600	-0.81300800
C	-8.37795200	-0.63467500	-0.79730300	H	-8.09015300	0.01765600	-1.61910900
H	-10.3058370	-1.07933200	-1.64767900	H	-10.9919730	-2.55874600	0.23170300
H	-9.43761700	-2.92126300	2.14094700	H	-7.22479300	-1.82073600	2.16779200
H	-5.55916900	-1.05745500	-2.13237700	H	-5.52079500	-2.73105900	-1.52425100
N	0.56715300	-1.99837800	1.61772600	C	0.68509600	-1.41929700	2.95917200
H	1.60074900	-0.82399000	3.03012100	H	-0.16858900	-0.75787100	3.13594300
H	0.69735700	-2.17172200	3.76792300	C	-0.68054600	-2.76731800	1.51851500
H	-1.52073500	-2.10601900	1.75089200	H	-0.81991800	-3.13925500	0.50070700
H	-0.72509900	-3.62043100	2.21742800	C	1.78689300	-2.74826300	1.21827100
H	2.62617300	-2.07647700	1.44843600	C	1.82998700	-3.04366500	-0.30614600
N	1.63650300	-1.82418000	-1.13268500	C	2.84487700	-1.00984300	-1.29727600
H	2.56565400	-0.04009100	-1.71728800	H	3.31658300	-0.82125100	-0.33033900

H	3.59374200	-1.46499000	-1.96872800	C	1.06302000	-2.14268100	-2.44398500
H	0.10122200	-2.64453800	-2.31763800	H	0.87503700	-1.21329200	-2.98997400
H	1.72505300	-2.77055700	-3.06808800	H	0.97259500	-3.68889300	-0.53539500
C	3.10715900	-3.83860100	-0.67489800	C	3.27334300	-5.12654500	0.13943300
C	3.28378900	-4.80253700	1.63576500	C	2.00386200	-4.05441100	2.02638000
H	2.01807600	-3.82286800	3.09772300	H	1.15103100	-4.72697600	1.86443900
H	3.37784400	-5.71808900	2.23352300	H	4.16358200	-4.18457000	1.86867200
H	4.19784600	-5.63920700	-0.15530900	H	2.44705200	-5.81913400	-0.07942300
H	3.09331300	-4.06652900	-1.74767100	H	3.98969800	-3.20922600	-0.50162300

Table A.2.35. 6a with (*S*,*S*)-TMCDA and TMEDA at –78 °C.







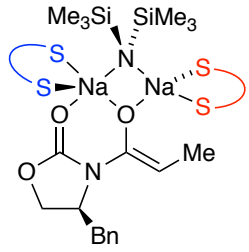
G = –2825.482974
G_{MP2} = –2824.506031

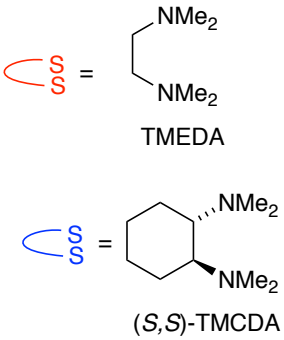
Na	0.00000000	0.00000000	0.00000000	O	-1.68560400	-1.21874700	-1.07344800
C	-2.89879900	-1.17643000	-0.93585600	O	-3.70754900	-1.94318200	-1.72570900
C	-5.07894700	-1.63307500	-1.43640300	C	-5.04863500	-0.91015800	-0.07813500
N	-3.65080900	-0.45844000	-0.04567700	C	-3.03648300	0.32044500	1.04868700
C	-3.61999200	0.22289800	2.27704900	H	-4.45395800	-0.45703700	2.42312600
C	-3.13352700	0.98901800	3.47493200	H	-2.80197700	0.32712800	4.28989200
H	-2.28331300	1.62154300	3.20270100	H	-3.91179100	1.63780000	3.90764900
O	-2.00982900	1.01805600	0.69936200	Na	-1.19643000	3.02140500	0.24381100
N	1.06098700	2.28421800	-0.21163200	Si	2.13348100	2.57041400	1.09092300
C	3.07520800	4.23633400	1.05227600	H	3.67850300	4.37119900	1.96020900
H	3.75788800	4.30011700	0.19567400	H	2.39014300	5.09151200	0.98198100

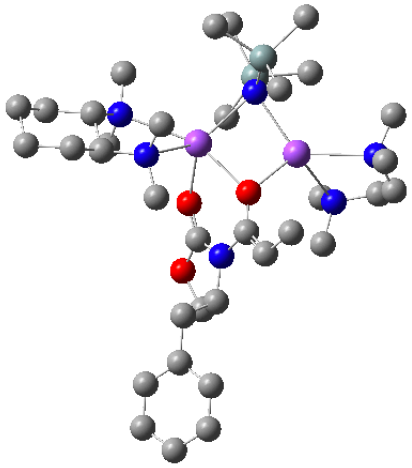
C	1.17757500	2.57525200	2.74876600	H	1.85103800	2.42810300	3.60329800
H	0.66875100	3.53491100	2.91116200	H	0.41416300	1.78794700	2.78585900
C	3.49524900	1.24237200	1.28616000	H	3.05829600	0.24507400	1.42526000
H	4.13343400	1.19519000	0.39531100	H	4.14256900	1.44406200	2.15026200
Si	1.42810600	2.64093300	-1.84540600	C	3.20747000	2.26114200	-2.43233200
H	3.32414500	2.48339600	-3.50162200	H	3.95179500	2.86002700	-1.89267700
H	3.47193700	1.20669200	-2.28565400	C	0.28553500	1.63488800	-3.00099800
H	0.56366600	0.57311600	-3.00104100	H	-0.76757700	1.67956000	-2.69351600
H	0.34282800	1.98520700	-4.03992300	C	1.17062300	4.48859500	-2.28477000
H	0.17564000	4.84192100	-1.98342100	H	1.90571700	5.11414000	-1.76256600
H	1.27856800	4.67834900	-3.36131500	N	-3.01270000	4.23214100	-1.20987800
C	-2.69865000	4.23392600	-2.64306200	H	-2.30979800	3.25248700	-2.92905600
H	-3.57252500	4.44640300	-3.28343500	H	-1.92488500	4.97680900	-2.85637000
C	-4.03020300	3.21050500	-0.93075900	H	-4.95937400	3.35451600	-1.50847300
H	-3.62171600	2.22682400	-1.17696300	H	-4.28007700	3.19413200	0.13314000
C	-3.35897100	5.59132700	-0.71940900	H	-2.58064400	6.25023900	-1.12865600
C	-3.30570300	5.70983200	0.82761200	N	-2.05348900	5.16451400	1.41475500
C	-0.86802000	6.00431000	1.19529300	H	-0.90095400	6.96245600	1.74022600
H	0.02104400	5.46305400	1.53317000	H	-0.74044800	6.21469600	0.12982200
C	-2.21058900	4.87250300	2.84468400	H	-1.31446600	4.36398700	3.21190800
H	-2.36000600	5.77345200	3.46480100	H	-3.06173600	4.20154700	2.99471700
H	-4.10734400	5.07752500	1.23231600	C	-3.61532800	7.16745600	1.25426000
H	-3.58961500	7.24314100	2.34756100	H	-2.82760500	7.83277600	0.87599300
C	-4.96656900	7.66486400	0.72682000	C	-5.01919300	7.55139000	-0.79931200
C	-4.72278400	6.11244700	-1.23877800	H	-4.74883700	6.04306600	-2.33225600
H	-5.52483500	5.46174300	-0.86502600	H	-5.99993300	7.86406100	-1.17901700
H	-4.27981300	8.23470000	-1.24241700	H	-5.13348100	8.70117600	1.04608200
H	-5.77887100	7.06724200	1.16606300	H	-5.22518700	-1.62916600	0.73517900
C	-6.08335800	0.22390400	0.02818600	H	-5.88186500	0.77515400	0.95225000
H	-5.92462100	0.91878700	-0.80502200	C	-7.50705300	-0.29254100	0.01503700
C	-8.04723100	-0.92340800	1.14628300	C	-9.34938700	-1.42260100	1.13574600
C	-10.1399280	-1.29727800	-0.00896400	C	-9.61816600	-0.66775600	-1.13932600
C	-8.31323200	-0.17085800	-1.12476700	H	-7.91836300	0.32705400	-2.00792800
H	-10.2267720	-0.55884000	-2.03325500	H	-11.1558530	-1.68275000	-0.01690000
H	-9.74963000	-1.90424700	2.02412000	H	-7.44392200	-1.01454500	2.04714400
H	-5.46454100	-0.98266100	-2.23105500	H	-5.65148900	-2.56178300	-1.42626300
N	0.34500900	-1.84856300	1.85834800	C	0.70915100	-1.27644900	3.15840800
H	1.64415500	-0.71536800	3.07359300	H	-0.07584600	-0.58836900	3.48491100
H	0.83569700	-2.05144200	3.93814200	C	-0.94598900	-2.53782100	1.98018000
H	-1.71204900	-1.82414300	2.29686400	H	-1.25378800	-2.94409000	1.01490500

H	-0.89968400	-3.36525800	2.71403100	C	1.39793000	-2.76348000	1.39064000
H	1.39396100	-3.69733900	1.98655800	H	2.36422200	-2.28352300	1.57694900
C	1.28958400	-3.14085000	-0.09020900	N	1.60573100	-2.04754300	-1.02135800
C	3.04892800	-1.80399000	-1.08510900	H	3.24858300	-0.97974700	-1.77494500
H	3.44022000	-1.51509500	-0.10740400	H	3.60526600	-2.69490700	-1.43576700
C	1.10374600	-2.37645800	-2.36134600	H	0.01528900	-2.46029100	-2.33378100
H	1.36878800	-1.57359400	-3.05613200	H	1.53584500	-3.31849700	-2.75003000
H	1.95112900	-4.01074500	-0.27264100	H	0.27142100	-3.47498900	-0.30873000

Table A.2.36. 6b with TMEDA and (*S*,*S*)-TMCDA at –78 °C.







G = –2825.481536

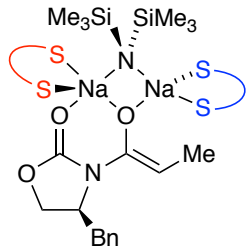
G_{MP2} = –2824.503779

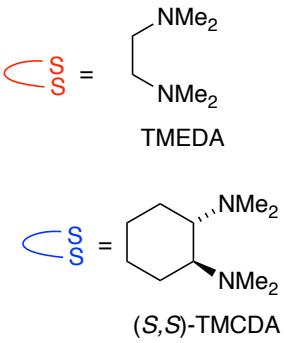
Na	0.00000000	0.00000000	0.00000000	O	-1.60889000	-0.71545200	-1.52068100
C	-2.61829700	-1.37197100	-1.32143900	O	-3.57236900	-1.46786200	-2.30361900
C	-4.55861200	-2.43195700	-1.89899700	C	-4.43403400	-2.47087100	-0.37147300
N	-3.02975300	-2.07051300	-0.21569700	C	-2.21632000	-2.32263300	0.98302700
C	-2.82723400	-2.94245400	2.03580700	H	-3.87346600	-3.21915600	1.98380500
C	-2.10898800	-3.23335700	3.32341700	H	-2.60171600	-2.76393100	4.18894700
H	-2.06025100	-4.31077700	3.55140700	H	-1.08399800	-2.85276700	3.28365100
O	-0.98711300	-1.93939800	0.90237900	Na	0.88787400	-3.04700300	0.41194800
N	2.27608800	-1.12425300	0.00413000	Si	3.01635900	-1.24925000	-1.53592200
C	4.35404600	0.05330600	-1.95178800	H	4.71874300	-0.07582800	-2.97976300
H	3.97388700	1.07826600	-1.86382800	H	5.22260600	-0.02811800	-1.28621500
C	3.90312900	-2.92870500	-1.80536800	H	4.30296600	-3.02481600	-2.82393600

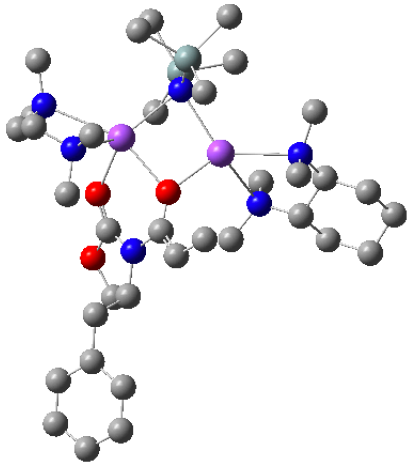
H	4.74237900	-3.04151800	-1.10750500	H	3.22512800	-3.77659700	-1.63735000
C	1.71468100	-1.11614700	-2.92756800	H	0.81036100	-1.69822700	-2.71173700
H	1.38818500	-0.07832500	-3.07550600	H	2.11796400	-1.46366400	-3.88799600
Si	3.11741000	-0.70878100	1.43590200	C	3.41911700	1.16742000	1.65265400
H	3.88663400	1.39555800	2.62004100	H	4.08218300	1.54930100	0.86619200
H	2.48273000	1.73617700	1.59512300	C	4.85020500	-1.49076900	1.66469900
H	4.82357400	-2.58534200	1.58773700	H	5.56311300	-1.13224200	0.91185200
H	5.26565400	-1.24012100	2.65027700	C	2.11339100	-1.27418500	2.96541300
H	2.43368800	-0.75347600	3.87734300	H	1.03552500	-1.10908800	2.84175500
H	2.25136600	-2.34867700	3.14881100	N	1.61963400	-5.25565300	1.59562400
C	3.07647400	-5.33537100	1.42559500	H	3.35313900	-5.22737900	0.37427200
H	3.55048700	-4.51862900	1.97607600	H	3.48485400	-6.29291800	1.79961100
C	1.28951800	-5.31744300	3.02533400	H	0.21185600	-5.19633500	3.16457300
H	1.60132400	-6.27398200	3.48384900	H	1.79394600	-4.50438600	3.55441400
C	0.93462900	-6.34692600	0.88314200	H	-0.09579600	-6.38623000	1.25043900
H	1.39184900	-7.32338600	1.13463900	C	0.93023400	-6.21277800	-0.64160400
N	0.20791000	-5.03626100	-1.14900700	C	0.45904400	-4.88052800	-2.58740500
H	-0.04722100	-3.98310000	-2.95357600	H	1.53032600	-4.76350700	-2.77025000
H	0.09647900	-5.74791900	-3.16957300	C	-1.23775100	-5.15110300	-0.91896500
H	-1.73815900	-4.28840900	-1.36466400	H	-1.65505500	-6.07206300	-1.36864800
H	-1.47323600	-5.14056600	0.14782200	H	1.95937100	-6.15532100	-1.01139500
H	0.50100300	-7.14517100	-1.05815800	H	-4.57598300	-3.48532600	0.00916900
C	-5.40637100	-1.49539300	0.34053700	H	-5.07676000	-1.39537700	1.37949600
H	-5.30279000	-0.50840300	-0.12742500	C	-6.84825600	-1.95025300	0.28095000
C	-7.76974100	-1.33502400	-0.57729600	C	-9.09310900	-1.77580300	-0.64742600
C	-9.51746700	-2.84418100	0.14282500	C	-8.61131500	-3.46474300	1.00603600
C	-7.29132600	-3.02028000	1.07371200	H	-6.59689600	-3.50246600	1.75881700
H	-8.93474500	-4.29240000	1.63198400	H	-10.5470380	-3.18790600	0.09162200
H	-9.79164000	-1.28076700	-1.31700800	H	-7.44994600	-0.49381500	-1.18899100
H	-5.53625900	-2.09798600	-2.25030700	H	-4.31800300	-3.39821400	-2.35869600
N	0.05316300	2.53004300	-0.95743800	C	-0.44201600	3.54977200	0.00334600
C	-1.61352200	3.02811400	0.87861700	N	-1.30000900	1.73966900	1.54742000
C	-2.51151800	1.00920300	1.93075600	H	-3.14698200	0.86330900	1.05153300
H	-2.23476800	0.02194000	2.30856300	H	-3.10535500	1.52235100	2.70878200
C	-0.40865900	1.85875800	2.70623400	H	-0.08913900	0.85872400	3.01432700
H	0.48699100	2.42907500	2.44703400	H	-0.88454500	2.33903100	3.57871300
H	-2.44989500	2.80509700	0.20250600	C	-2.09178900	4.13110100	1.85684100
H	-2.94118900	3.75691900	2.44084000	H	-1.29070300	4.34782000	2.57593100
C	-2.46882400	5.44032200	1.15434600	H	-2.78718300	6.18396900	1.89593600
H	-3.32833500	5.27453400	0.48805200	C	-1.28311000	5.95980400	0.33675700

C	-0.82573300	4.89428200	-0.66584600	H	0.02432800	5.26558000	-1.25036400
H	-1.64254600	4.72179100	-1.37902100	H	-1.54882600	6.88304700	-0.19359900
H	-0.45595200	6.21499200	1.01559500	H	0.40442200	3.74973400	0.67435300
C	1.41946800	2.81886000	-1.40194900	H	1.78193300	1.98728600	-2.01235800
H	1.50011800	3.73909800	-2.00866400	H	2.08276800	2.91299300	-0.53749400
C	-0.81567300	2.32632100	-2.12476400	H	-0.48525300	1.43750700	-2.66814500
H	-1.84472400	2.13975100	-1.80926900	H	-0.80814200	3.17890600	-2.82521700

Table A.2.37. 6b with (*S*,*S*)-TMCDA and TMEDA at –78 °C.







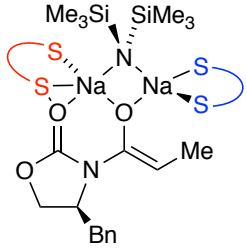
G = –2825.48261
G_{MP2} = –2824.506047

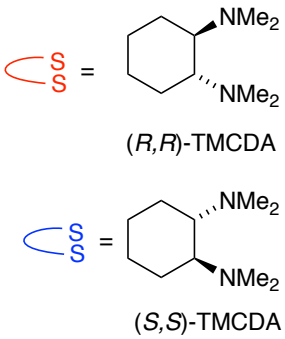
Na	0.00000000	0.00000000	0.00000000	O	1.85919400	0.37922400	-1.34735700
C	2.73430400	1.22535400	-1.24294900	O	3.68126200	1.35666300	-2.22618500
C	4.48965300	2.51090700	-1.93181100	C	4.33706600	2.68219100	-0.41624900
N	2.99583000	2.11271700	-0.23447300	C	2.08204400	2.43083600	0.87377800
C	2.61140000	3.09398600	1.94410100	H	3.66659800	3.33887500	1.97003700
C	1.79348200	3.47437000	3.14591100	H	2.25266600	3.11947300	4.08063400
H	1.67210600	4.56405300	3.26175900	H	0.79362000	3.03423500	3.08355800
O	0.85820600	2.06708800	0.69349500	Na	-1.08932400	3.05296700	0.19675600
N	-2.28957400	0.98896300	-0.15862200	Si	-2.89619600	0.94686200	-1.75819100
C	-3.89277000	-0.61025300	-2.24455900	H	-4.19177900	-0.57591300	-3.30074500
H	-3.30598800	-1.52566100	-2.09720800	H	-4.80864400	-0.71243600	-1.64907400
C	-4.06064700	2.41173700	-2.17179500	H	-4.35057100	2.42047000	-3.23125800
H	-4.98126000	2.35388300	-1.57748500	H	-3.59190200	3.37999300	-1.95040500
C	-1.45508200	1.03498800	-3.01008800	H	-0.74202300	1.83747400	-2.77948500

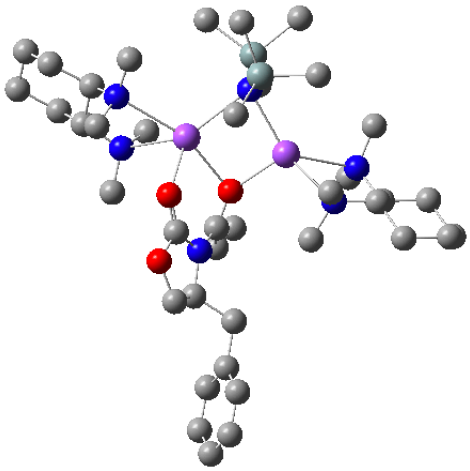
H	-0.87415400	0.10416100	-3.01659100	H	-1.81924800	1.19937300	-4.03291000
Si	-3.17083000	0.51255700	1.22798800	C	-3.19596900	-1.37740000	1.52206600
H	-3.72668200	-1.63687900	2.44808100	H	-3.69124700	-1.90148700	0.69544200
H	-2.17795600	-1.78087100	1.59873500	C	-5.00997100	1.03629300	1.28219100
H	-5.13107800	2.11742600	1.13936400	H	-5.59617200	0.53942700	0.49858700
H	-5.46814600	0.77561000	2.24583700	C	-2.37541500	1.25413400	2.80404600
H	-2.72625400	0.74240700	3.70988600	H	-1.28057100	1.18003500	2.78040100
H	-2.62846000	2.31608400	2.92465400	N	-2.21785900	5.21712600	1.12166900
C	-3.64641000	4.93840100	1.31073200	H	-4.12789900	4.79043900	0.33928500
H	-3.76258500	4.01545300	1.88522000	H	-4.18157800	5.73881200	1.85149500
C	-1.53907900	5.28439900	2.42320800	H	-0.48158500	5.52761800	2.29130900
H	-1.98387600	6.02035800	3.11333100	H	-1.59347400	4.30456500	2.90740100
C	-2.00108800	6.41188000	0.25964400	H	-2.75838900	6.33693100	-0.53182300
C	-0.61025900	6.40167300	-0.42973800	N	-0.35975400	5.14021000	-1.17605000
C	-1.07634300	5.04188500	-2.45404100	H	-0.98534800	4.02210500	-2.83859300
H	-2.14089500	5.24784500	-2.31588000	H	-0.68774600	5.72540700	-3.22764200
C	1.07181000	4.90223500	-1.38835000	H	1.20570100	3.91258600	-1.83512800
H	1.54333300	5.64319700	-2.05882200	H	1.59622100	4.90649200	-0.42804900
H	0.14931300	6.42269600	0.36362500	C	-0.41620500	7.67545900	-1.29064800
H	0.58995100	7.66891300	-1.72625500	H	-1.12000900	7.65423400	-2.13307000
C	-0.64718000	8.97497100	-0.51160300	H	-0.50614300	9.83740800	-1.17500000
H	0.09980900	9.07054800	0.29030300	C	-2.05127600	8.97998700	0.09847300
C	-2.23746700	7.75301100	0.99813900	H	-3.24215000	7.75403400	1.43730900
H	-1.53151400	7.83505200	1.83490700	H	-2.22177900	9.89575900	0.67818500
H	-2.80109900	8.97430500	-0.70631400	H	4.33318300	3.73532000	-0.12462800
C	5.42359400	1.90994800	0.37842300	H	5.10349000	1.84988100	1.42306400
H	5.45836000	0.88233400	-0.00405000	C	6.79234900	2.54778700	0.27923900
C	7.79737100	1.98953400	-0.52230900	C	9.05141600	2.59470200	-0.62995900
C	9.32095000	3.77384000	0.06494900	C	8.33024700	4.34021100	0.87065300
C	7.07998000	3.73168800	0.97608400	H	6.31930900	4.17541600	1.61538200
H	8.53366100	5.25430100	1.42247900	H	10.2964690	4.24579500	-0.01522200
H	9.81725400	2.14132800	-1.25386100	H	7.59931200	1.06396000	-1.05881400
H	5.51271400	2.30680800	-2.25135300	H	4.09629200	3.36976000	-2.48874900
N	0.22305600	-2.57996300	-0.94401700	C	1.34004600	-3.06777100	-0.12179000
C	1.14521100	-2.88119500	1.38650700	N	1.18368300	-1.47948000	1.83118100
C	2.55510700	-0.95684700	1.83004800	H	2.97044900	-0.98039600	0.82028000
H	2.55074800	0.08485500	2.16141300	H	3.21684900	-1.54095100	2.49819000
C	0.61813100	-1.35286200	3.17783900	H	0.63295100	-0.30170900	3.47954700
H	-0.42056800	-1.69567300	3.18168300	H	1.18240200	-1.93727000	3.92901000
H	0.17958400	-3.30065500	1.68623900	H	1.91800900	-3.47749800	1.90993800

H	2.24102500	-2.53664800	-0.44355400	H	1.52413700	-4.14385800	-0.31259600
C	-0.94425400	-3.45904500	-0.83605900	H	-1.75376100	-3.06512300	-1.45613900
H	-0.71941400	-4.49049400	-1.17009900	H	-1.31033000	-3.49998600	0.19186500
C	0.64125400	-2.49274400	-2.34893000	H	-0.20172700	-2.15165700	-2.95758800
H	1.44974300	-1.76524700	-2.44705100	H	0.97565500	-3.47016900	-2.74615100

Table A.2.38. 6a with (*S*,*S*)-TMCDA and (*R*,*R*)-TMCDA at –78 °C.







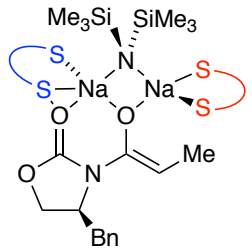
G = –2980.979088
G_{MP2} = –2979.90941

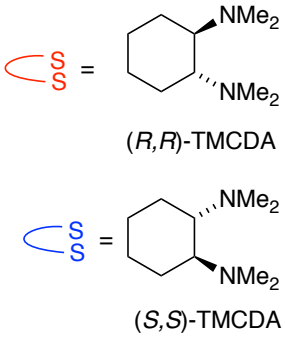
Na	0.00000000	0.00000000	0.00000000	O	1.11116300	1.59101300	-1.25982000
C	2.12807800	2.22140600	-1.02220000	O	2.52969400	3.21589600	-1.86925700
C	3.79820200	3.72650500	-1.43883400	C	3.97007500	3.22213500	0.00622000
N	3.00369900	2.11553300	0.02923800	C	2.72454400	1.27104500	1.20708500
C	3.08906900	1.76348800	2.42582800	H	3.49726500	2.76612200	2.50314800
C	2.90840100	0.99242400	3.70352500	H	2.20648800	1.48254700	4.39597000
H	2.51409500	-0.00621600	3.49335100	H	3.85175000	0.87276800	4.25906300
O	2.16647800	0.13850800	0.94082200	Na	2.50724800	-2.01274500	0.59348400
N	0.21273500	-2.54812900	0.00701800	Si	-0.62037600	-3.30398800	1.29861400
C	-0.51819400	-5.21581500	1.36149800	H	-1.00117800	-5.60416300	2.26840100
H	-1.01760900	-5.68236300	0.50321900	H	0.51974100	-5.57332000	1.36310000
C	0.06677800	-2.72807800	2.98874500	H	-0.59650800	-3.03572000	3.80796600
H	1.05046800	-3.16938100	3.19773900	H	0.18077400	-1.63933600	3.04492900
C	-2.49460200	-2.92765500	1.36191500	H	-2.68899400	-1.84933500	1.43050200
H	-3.00164700	-3.29543100	0.46102900	H	-2.97268700	-3.40419400	2.22822500

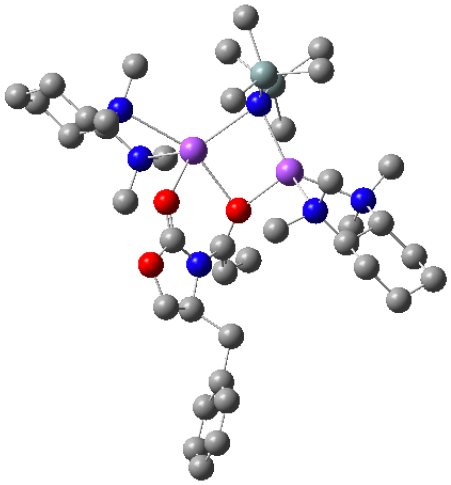
Si	0.23806100	-3.17776700	-1.58692400	C	-1.39603100	-3.90775900	-2.26152100
H	-1.27867100	-4.21615500	-3.30926300	H	-1.70831200	-4.79505500	-1.69646900
H	-2.22238400	-3.18886200	-2.22089400	C	0.74520000	-1.81362600	-2.82791000
H	-0.07003800	-1.09769600	-2.99738000	H	1.60388200	-1.22522000	-2.47929700
H	1.00709900	-2.23727400	-3.80646500	C	1.49795000	-4.60736700	-1.80173000
H	2.49382400	-4.33368200	-1.43003000	H	1.17259000	-5.48910200	-1.23520500
H	1.60741000	-4.90968700	-2.85214700	N	4.78546200	-2.22513300	-0.70709800
C	4.60387400	-2.40890300	-2.15163000	H	3.79545200	-1.75925600	-2.49975900
H	5.50490400	-2.16643100	-2.74116300	H	4.31957700	-3.44286000	-2.36545800
C	5.17966200	-0.83729900	-0.43707600	H	6.11204900	-0.54307000	-0.94944200
H	4.38073900	-0.17142800	-0.77318800	H	5.30471900	-0.67081400	0.63567000
C	5.69441500	-3.24690600	-0.12605100	H	5.31579900	-4.21015100	-0.49626600
C	5.64338900	-3.28615000	1.42489700	N	4.25796200	-3.35582400	1.96327000
C	3.63573500	-4.68189900	1.84685300	H	4.09764300	-5.44229300	2.49813200
H	2.58005000	-4.60842600	2.12385900	H	3.68107100	-5.03580500	0.81305100
C	4.19602100	-2.88497300	3.35227200	H	3.15236400	-2.84962300	3.67840900
H	4.74470600	-3.52978500	4.06075800	H	4.60154400	-1.87079100	3.41781100
H	6.04263500	-2.33002100	1.78807100	C	6.57756500	-4.39986400	1.96120700
H	6.54429400	-4.40857300	3.05703500	H	6.20732600	-5.37880900	1.62909600
C	8.02510800	-4.24270700	1.48016200	C	8.07552700	-4.21909200	-0.04951700
C	7.16532200	-3.11451500	-0.59936400	H	7.19899500	-3.11631000	-1.69471200
H	7.56214000	-2.14269600	-0.27607300	H	9.10296200	-4.06605700	-0.40278700
H	7.75287900	-5.19512100	-0.44087800	H	8.64143600	-5.05869500	1.87767400
H	8.44966400	-3.30814600	1.87556600	H	3.65767700	3.99957200	0.71807100
C	5.41928800	2.80734800	0.32303300	H	5.42565800	2.31468900	1.30029400
H	5.73602900	2.06290500	-0.41678100	C	6.36942600	3.98699300	0.31505300
C	6.35055500	4.92399600	1.35981200	C	7.20675400	6.02462800	1.35169200
C	8.10355500	6.20832800	0.29665700	C	8.13748000	5.28222700	-0.74610600
C	7.27653700	4.18270100	-0.73490100	H	7.31588400	3.46093200	-1.54806400
H	8.83582800	5.41192900	-1.56883200	H	8.77361500	7.06376100	0.29103000
H	7.17851800	6.73626600	2.17277400	H	5.66482800	4.78302400	2.19269500
H	4.57685700	3.32833700	-2.10074000	H	3.78395400	4.81448600	-1.52226000
N	-2.41632700	0.76654300	-0.91335700	C	-3.30072500	1.19679300	0.19986100
C	-2.63495000	2.25636300	1.11785700	N	-1.26637300	1.87927900	1.54605900
C	-1.20867600	0.97600400	2.69815700	H	-1.84093700	0.09874500	2.52964500
H	-0.17633900	0.63316400	2.82109800	H	-1.51923500	1.44501900	3.64839700
C	-0.42806700	3.05680300	1.78256200	H	0.58847100	2.73649200	2.03127500
H	-0.38046100	3.66382500	0.87218300	H	-0.79503000	3.69683600	2.60707100
H	-2.50910600	3.16492300	0.51559200	C	-3.57843000	2.62779100	2.28811700
C	-4.94349800	3.13268400	1.80673400	C	-5.60875600	2.08396200	0.91045700

C	-4.69059500	1.70982900	-0.26003700	H	-4.55801900	2.59449700	-0.89781900
H	-5.17727900	0.94897500	-0.88015500	H	-6.56941100	2.45207400	0.52829500
H	-5.83271200	1.18639900	1.50559100	H	-4.81513200	4.06815000	1.24220600
H	-5.58174400	3.37109800	2.66707100	H	-3.73730700	1.74735400	2.92497400
H	-3.09348000	3.38471400	2.91712000	H	-3.46772100	0.29009000	0.79908100
C	-2.97150100	-0.37822800	-1.64044400	H	-2.21065700	-0.77683600	-2.31720100
H	-3.24470000	-1.16920800	-0.93690100	H	-3.85796500	-0.12825200	-2.24983100
C	-2.05955200	1.82980800	-1.86010100	H	-1.57130100	2.65767400	-1.34369500
H	-1.33478400	1.43482800	-2.57714400	H	-2.92413400	2.21821300	-2.42621800

Table A.2.39. 6a with (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA at –78 °C.







G = –2980.981237

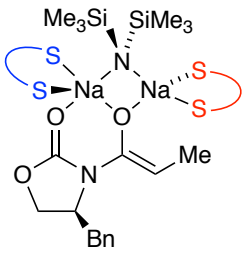
G_{MP2} = –2979.912354

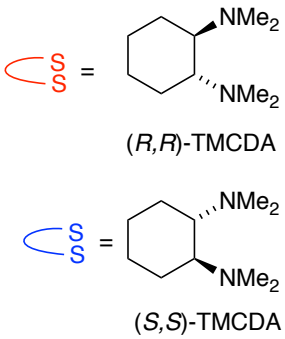
Na	0.00000000	0.00000000	0.00000000	O	1.28110900	1.46211700	-1.30869400
C	2.35181300	2.00458400	-1.08529400	O	2.86432700	2.90651800	-1.97566500
C	4.16985900	3.31304400	-1.54093700	C	4.25919100	2.87919500	-0.06570000
N	3.19181800	1.87173300	-0.01210800	C	2.81103000	1.10278800	1.19264600
C	3.14803600	1.64817400	2.39603900	H	3.60772500	2.63141700	2.42624200
C	2.87480000	0.97821600	3.71328600	H	2.16547000	1.54694100	4.33447400
H	2.44735200	-0.01584500	3.55736100	H	3.78605400	0.86133300	4.31982800
O	2.20153900	-0.00843900	0.95210400	Na	2.35392300	-2.14237400	0.35922300
N	0.00193300	-2.57877200	0.07459000	Si	-0.73110300	-3.06558200	1.54742000
C	-0.80505300	-4.95074600	1.86758000	H	-1.20502900	-5.16087500	2.86882500
H	-1.44485700	-5.47258700	1.14525600	H	0.19199100	-5.40627400	1.80744300

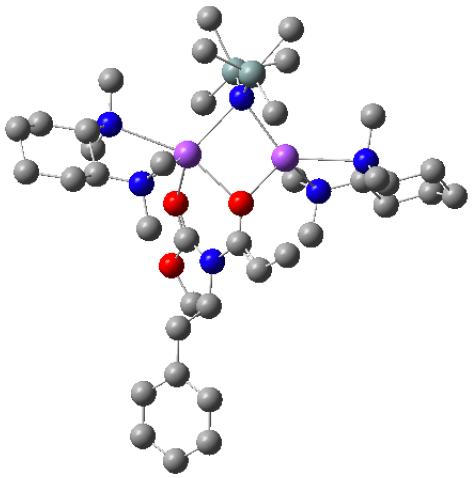
C	0.23293500	-2.35941600	3.04036400	H	-0.37767700	-2.35957400	3.95273700
H	1.12185200	-2.96884800	3.25516300	H	0.57752300	-1.33434000	2.86181300
C	-2.53489900	-2.46086800	1.74587900	H	-2.59990900	-1.36856800	1.66009100
H	-3.18196800	-2.88720900	0.96916100	H	-2.95578500	-2.74197900	2.72065700
Si	-0.21985100	-3.43442500	-1.39331200	C	-1.99707900	-4.01221200	-1.80524500
H	-2.03016100	-4.48498000	-2.79623000	H	-2.35643900	-4.75418200	-1.08102200
H	-2.72147400	-3.18901800	-1.80995400	C	0.32531100	-2.35513800	-2.87529900
H	-0.38703400	-1.54159700	-3.06437100	H	1.30237800	-1.88240000	-2.70879700
H	0.39588200	-2.94243600	-3.80035500	C	0.81676700	-5.04423800	-1.49719400
H	1.87037600	-4.87175700	-1.24178800	H	0.43439800	-5.79448800	-0.79402100
H	0.78831200	-5.48840000	-2.50158400	N	4.39406600	-2.34185500	-1.20911500
C	4.21349400	-3.41052200	-2.20008600	H	3.22527700	-3.30820600	-2.65619400
H	4.96129400	-3.38453100	-3.01024800	H	4.25658800	-4.39285200	-1.72291100
C	4.36314400	-1.03824000	-1.88085900	H	5.17486700	-0.90349900	-2.61775200
H	3.41309600	-0.92969000	-2.41424900	H	4.41634900	-0.23884300	-1.13816600
C	5.59682900	-2.49886200	-0.34482400	H	5.68624900	-1.54884200	0.20023600
C	5.41911200	-3.62393500	0.71084700	N	4.19328000	-3.44149100	1.53721800
C	3.68155300	-4.72104000	2.04146400	H	4.37112700	-5.22344200	2.74299400
H	2.73716400	-4.55229000	2.56816500	H	3.48232900	-5.39810300	1.20479100
C	4.34379400	-2.48452100	2.64414600	H	3.36103300	-2.29012800	3.08265400
H	5.00326200	-2.84777200	3.44940300	H	4.72933100	-1.52917900	2.27772100
H	5.26160700	-4.56136700	0.16194800	C	6.70531300	-3.80187400	1.55521100
C	7.96060000	-4.02684800	0.70518300	C	8.14860100	-2.85953000	-0.26656300
C	6.90559700	-2.70403300	-1.14996400	H	6.81143000	-3.60780000	-1.76632600
H	7.03934800	-1.86744400	-1.84579400	H	9.03467100	-3.01322800	-0.89512700
H	8.32473900	-1.93475800	0.30252800	H	7.87047100	-4.96541000	0.13870800
H	8.83634300	-4.13742500	1.35675900	H	6.86683000	-2.90379600	2.16515700
H	6.56514200	-4.63354300	2.25645300	H	4.00633500	3.72358200	0.59146300
C	5.65031000	2.34556100	0.32332300	H	5.57879200	1.92336800	1.33086700
H	5.90864700	1.52308500	-0.35481200	C	6.71563000	3.42049600	0.26640000
C	6.77571500	4.41887800	1.25096900	C	7.73788800	5.42666000	1.19198200
C	8.66326200	5.45344700	0.14592900	C	8.61928100	4.46414500	-0.83666400
C	7.65273000	3.45822500	-0.77476700	H	7.63156500	2.68572300	-1.54060700
H	9.33878300	4.47159700	-1.65129000	H	9.41529100	6.23650100	0.10109900
H	7.76926300	6.18836600	1.96667400	H	6.06741100	4.39917400	2.07655900
H	4.91756400	2.80180700	-2.15927000	H	4.26681100	4.39023900	-1.68562800
N	-1.28649900	1.76442600	1.47580800	C	-2.67311700	2.02982900	1.00846500
C	-2.75994100	2.18634400	-0.53439500	N	-2.13736700	1.05156400	-1.26307900
C	-2.98814700	-0.13881600	-1.36438700	H	-2.38626400	-0.97395100	-1.73083900
H	-3.84187300	-0.01140300	-2.05235100	H	-3.37390600	-0.42165000	-0.38191200

C	-1.67283900	1.45174600	-2.59518200	H	-0.95149000	2.26719500	-2.50784800
H	-1.15527600	0.60946800	-3.06424400	H	-2.49282200	1.75982900	-3.26946400
H	-2.16334600	3.06682100	-0.80508200	C	-4.21740500	2.47649300	-0.97281500
H	-4.24643900	2.61584300	-2.06035400	H	-4.84456600	1.60233000	-0.75397100
C	-4.82805900	3.69088200	-0.26518000	C	-4.78110500	3.49211000	1.25200300
C	-3.34003700	3.24096600	1.71083200	H	-3.31400200	3.09295700	2.79656100
H	-2.75266800	4.14596300	1.50617500	H	-5.19166600	4.36614100	1.77346600
H	-5.41570600	2.63677900	1.52746100	H	-5.85978900	3.84323700	-0.60685000
H	-4.27149100	4.60120500	-0.53327300	H	-3.24619100	1.13266600	1.28257900
C	-1.25147500	1.28268700	2.86074400	H	-1.91559100	0.42052100	2.97395400
H	-0.23338600	0.96303800	3.10152600	H	-1.54508600	2.04652900	3.60247300
C	-0.36806200	2.90163800	1.32594900	H	0.63792700	2.58161800	1.61351000
H	-0.32987600	3.22707200	0.28360600	H	-0.63688800	3.76539400	1.95807500

Table A.2.40. 6b with (*S*,*S*)-TMCDA and (*R*,*R*)-TMCDA at –78 °C.







G = –2980.980203

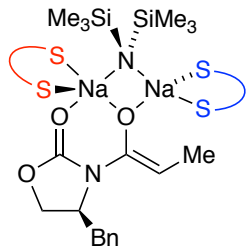
G_{MP2} = –2979.910211

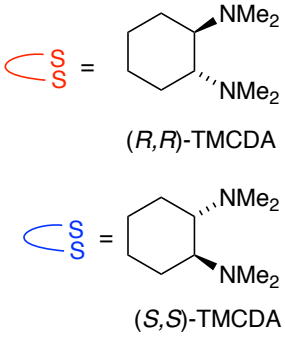
Na	0.00000000	0.00000000	0.00000000	O	0.31374200	1.75013400	-1.50306600
C	0.36107100	2.94801500	-1.27169700	O	0.75344300	3.81841400	-2.25739800
C	0.55020100	5.16440100	-1.79293500	C	0.56759500	5.03361100	-0.26581300
N	0.10011600	3.64899600	-0.12223800	C	-0.51915900	3.09330600	1.09081700
C	-0.55853900	3.89080200	2.19776200	H	-0.12431700	4.88355000	2.17886400
C	-1.17594900	3.44115900	3.49222200	H	-0.45575700	3.45802200	4.32492900
H	-2.01778600	4.07939300	3.80544700	H	-1.54986200	2.41708300	3.40290700

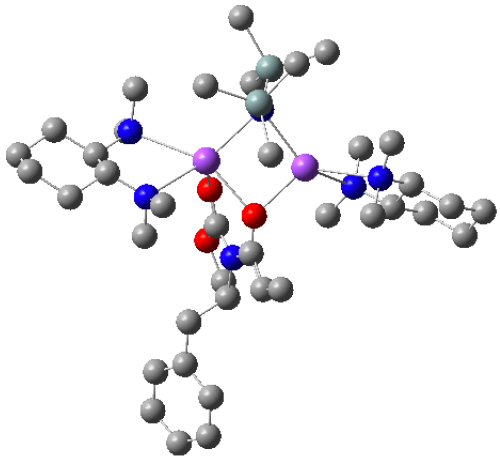
O	-0.98801900	1.89770400	0.96265600	Na	-3.00664900	1.06813800	0.50127400
N	-2.26140000	-1.19254200	0.06264100	Si	-2.82499300	-1.72364100	-1.46614700
C	-2.58056900	-3.57517000	-1.88256200	H	-2.89712500	-3.78385900	-2.91351700
H	-1.53283000	-3.88640900	-1.79245300	H	-3.17057400	-4.22523900	-1.22477800
C	-4.70690800	-1.44079900	-1.70554800	H	-5.04153600	-1.73535000	-2.70941300
H	-5.28194600	-2.02810800	-0.97817900	H	-4.98196200	-0.38680400	-1.56356500
C	-1.96856500	-0.77058300	-2.88403500	H	-1.86934200	0.30086700	-2.67346700
H	-0.95346000	-1.14726500	-3.06563300	H	-2.52117300	-0.87772900	-3.82698700
Si	-2.33236100	-2.14325700	1.48494800	C	-0.92063900	-3.42509400	1.64212900
H	-0.95994100	-3.95634500	2.60265300	H	-0.98564800	-4.17613300	0.84501000
H	0.06634200	-2.95194600	1.56506000	C	-3.92450500	-3.17378000	1.75068300
H	-4.83255900	-2.55919500	1.70462100	H	-4.03070600	-3.96179400	0.99499000
H	-3.90973600	-3.66497400	2.73314000	C	-2.20347900	-1.02200100	3.03268700
H	-1.88685600	-1.59047100	3.91697200	H	-1.49507300	-0.19605700	2.89091100
H	-3.17592000	-0.57365300	3.27996000	N	-5.22935000	1.78425700	1.67999200
C	-5.89079800	0.47373600	1.60987100	H	-6.11442600	0.21178800	0.57235900
H	-5.21379400	-0.28960000	2.00315200	H	-6.82458200	0.42329000	2.19423800
C	-4.95340500	2.13361700	3.07841900	H	-4.38351300	3.06641900	3.12456500
H	-5.86571400	2.24816200	3.69050000	H	-4.34419700	1.34782600	3.53520500
C	-5.96222900	2.87272700	0.97782500	H	-5.53161700	3.80563300	1.36366900
C	-5.73355000	2.86466100	-0.55852400	N	-4.29327600	2.80434700	-0.92134200
C	-4.09014900	2.50826900	-2.34444000	H	-3.02958600	2.30338100	-2.52081200
H	-4.65718200	1.61658500	-2.62656200	H	-4.38570300	3.33513100	-3.01296700
C	-3.52212600	3.99756000	-0.55146100	H	-2.46960500	3.81523200	-0.78037000
H	-3.83425800	4.90641100	-1.09374700	H	-3.58930900	4.18901800	0.52204000
H	-6.16869300	1.93623200	-0.95504900	C	-6.49112900	4.04939700	-1.21165900
H	-6.04746000	4.99481800	-0.87135900	H	-6.35571200	4.01528600	-2.29850400
C	-7.98649500	4.06670500	-0.87498900	H	-8.46576700	4.93175500	-1.35022200
H	-8.47168600	3.17216700	-1.29243100	C	-8.19398300	4.09572600	0.64190700
C	-7.47691200	2.90940000	1.29674600	H	-7.94775900	1.98349500	0.94123600
H	-7.61911400	2.93461800	2.38391300	H	-9.26257000	4.06869500	0.88926900
H	-7.80218600	5.03988500	1.04830500	H	-0.14787600	5.71532800	0.20052400
C	1.97842200	5.24633700	0.34129500	H	1.95859800	4.87879200	1.37185100
H	2.68631300	4.61627100	-0.21156400	C	2.42613100	6.69121200	0.30088400
C	3.37586700	7.13279400	-0.63032600	C	3.76575700	8.47296000	-0.68017000
C	3.20896200	9.39702700	0.20415300	C	2.26367400	8.97095200	1.14025600
C	1.87829100	7.63162900	1.18703400	H	1.14985300	7.30832300	1.92804700
H	1.83020200	9.68177700	1.83902700	H	3.51215400	10.4399200	0.16891700
H	4.50742800	8.79205000	-1.40780800	H	3.82377000	6.41673800	-1.31635300
H	1.34968700	5.79249200	-2.18911600	H	-0.41563000	5.52503400	-2.16675400

N	1.96028300	-1.56500100	-1.00167800	C	3.07039700	-1.81865200	-0.04685100
C	3.44826400	-0.56332600	0.78348900	N	2.27717400	0.07901700	1.43168400
C	2.52429300	1.49487100	1.71700200	H	2.78710400	2.01601600	0.79076300
H	1.61455300	1.95325300	2.11336800	H	3.33573500	1.65945700	2.44955900
C	1.80623600	-0.59620000	2.64594800	H	0.84284500	-0.16776600	2.93915300
H	1.65602700	-1.66278900	2.45943100	H	2.49299100	-0.48902500	3.50339800
H	3.83313200	0.18575300	0.07877100	C	4.59709700	-0.89411700	1.76942800
H	4.86590200	0.00875900	2.33071700	H	4.24182800	-1.62567800	2.50732000
C	5.83471700	-1.47424200	1.07615200	H	6.60977800	-1.69942900	1.81969900
H	6.26443000	-0.72773300	0.39179400	C	5.45588200	-2.73054800	0.28756800
C	4.33745400	-2.41472200	-0.71302100	H	4.06662400	-3.31923300	-1.26966000
H	4.72665400	-1.70006200	-1.45059400	H	6.32715500	-3.13634000	-0.24205600
H	5.12185900	-3.51228500	0.98568900	H	2.68050000	-2.57176300	0.65214500
C	1.35472900	-2.81378400	-1.47313000	H	0.45796200	-2.58229400	-2.05360300
H	2.02394300	-3.41214400	-2.11717900	H	1.05197800	-3.42704600	-0.62010900
C	2.32485600	-0.72583200	-2.15092000	H	1.41814600	-0.45149900	-2.69659400
H	2.78669000	0.20566800	-1.81611500	H	3.00916100	-1.22767400	-2.85648400

Table A.2.41. 6b with (*R*,*R*)-TMCDA and (*S*,*S*)-TMCDA at –78 °C.







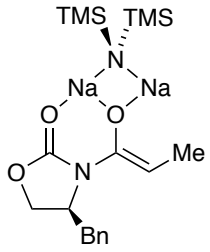
G = –2980.981324
G_{MP2} = –2979.910697

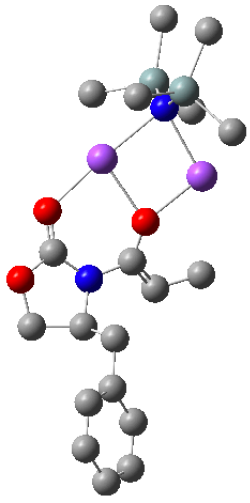
Na	0.00000000	0.00000000	0.00000000	O	0.31656300	1.73190400	-1.52871500
C	0.47625300	2.91614900	-1.27656900	O	0.99524000	3.75165500	-2.23395400
C	0.89745200	5.10712100	-1.76572600	C	0.82437800	4.96803900	-0.24054100

N	0.23884600	3.62584400	-0.12967900	C	-0.45566200	3.11215100	1.06231100
C	-0.51995600	3.93738100	2.14906100	H	-0.07187100	4.92340400	2.12179700
C	-1.16013400	3.51987200	3.44303400	H	-0.45930100	3.58840800	4.28918500
H	-2.02670200	4.14377900	3.71426000	H	-1.50338000	2.48313000	3.38291600
O	-0.94432100	1.92312100	0.94706300	Na	-2.96945900	1.08187400	0.42454600
N	-2.23386800	-1.19578900	0.07716100	Si	-2.80094600	-1.77026400	-1.43512200
C	-2.44174400	-3.60381300	-1.85160600	H	-2.78817200	-3.84359800	-2.86606400
H	-1.37184000	-3.84226700	-1.80687300	H	-2.95476200	-4.28778300	-1.16404700
C	-4.70098100	-1.61872900	-1.63882800	H	-5.02917500	-1.91093500	-2.64561600
H	-5.21665300	-2.26922200	-0.92117900	H	-5.05555100	-0.59500000	-1.46190900
C	-2.02076500	-0.77283900	-2.86762800	H	-1.98388700	0.30619000	-2.67051700
H	-0.98417300	-1.08637200	-3.04865000	H	-2.56841400	-0.92485900	-3.80721600
Si	-2.33190800	-2.11155800	1.52266000	C	-0.90523400	-3.36800300	1.73964000
H	-0.98330000	-3.91190700	2.69067800	H	-0.90946900	-4.10960800	0.93116100
H	0.07373800	-2.87208100	1.72206900	C	-3.92127100	-3.14957200	1.76801100
H	-4.82817300	-2.53521300	1.70055600	H	-4.01298600	-3.94498400	1.01809200
H	-3.92193000	-3.63113000	2.75530600	C	-2.25317000	-0.96131300	3.05146500
H	-1.93885200	-1.50879000	3.94980300	H	-1.55607700	-0.12716600	2.90584700
H	-3.23809200	-0.52976900	3.27633800	N	-5.23341100	1.73901600	1.49175200
C	-5.97461800	0.51265300	1.80754600	H	-6.28698000	0.01912800	0.88231500
H	-5.32088200	-0.17694300	2.34894200	H	-6.86752600	0.68888400	2.43304600
C	-4.69760800	2.33880500	2.72142300	H	-4.16408400	3.26558000	2.49455100
H	-5.47048300	2.55591500	3.47761200	H	-3.97882500	1.64874500	3.17336900
C	-6.04114600	2.67132000	0.65881400	H	-6.58495200	2.03002800	-0.04726700
C	-5.15808900	3.63415600	-0.18025900	N	-4.13923300	2.91172100	-0.98732700
C	-4.67215000	2.25452200	-2.18816000	H	-3.90378200	1.59857200	-2.60759300
H	-5.53592400	1.63370200	-1.93760700	H	-4.97200300	2.96481700	-2.97679500
C	-3.01855000	3.78226300	-1.35855200	H	-2.25427600	3.18033400	-1.85885600
H	-3.30783800	4.59781300	-2.04569500	H	-2.57487600	4.21752600	-0.45842500
H	-4.58309900	4.24990500	0.52482900	C	-6.04234400	4.58931900	-1.01956100
H	-5.40220000	5.28539200	-1.57456300	H	-6.59280400	4.00640000	-1.76977300
C	-7.06161400	5.36435900	-0.17726700	H	-7.66340800	6.01453600	-0.82452000
H	-6.53857500	6.02407600	0.53070000	C	-7.95487300	4.39070800	0.59745100
C	-7.09704600	3.46485700	1.46784800	H	-7.73550100	2.76429700	2.01958200
H	-6.58804800	4.08151300	2.22010200	H	-8.67060800	4.93444600	1.22661300
H	-8.54970900	3.79643700	-0.11171500	H	0.14419500	5.70775800	0.18876500
C	2.21216500	5.06370400	0.44415300	H	2.10165500	4.70652800	1.47280800
H	2.89304900	4.37144400	-0.06652700	C	2.78346700	6.46453100	0.42724400
C	3.82037400	6.81674700	-0.44738100	C	4.32712100	8.11787900	-0.47585800
C	3.80189600	9.09201900	0.37339100	C	2.77052500	8.75495800	1.25317300

C	2.26856400	7.45421800	1.27886900	H	1.47368700	7.19917900	1.97693300
H	2.36049600	9.50489800	1.92467400	H	4.19575200	10.1046000	0.35474600
H	5.13477800	8.36721200	-1.15914400	H	4.24386100	6.06032900	-1.10501800
H	1.77199200	5.65928500	-2.11363600	H	-0.00892700	5.56108400	-2.18417100
N	2.08264100	-0.17811300	1.61089100	C	3.05388500	-1.23053800	1.21661300
C	3.33647300	-1.23586700	-0.31029500	N	2.09513100	-1.27029000	-1.12444600
C	1.49158900	-2.60166600	-1.24683100	H	0.49840300	-2.50217600	-1.69304900
H	2.07522900	-3.29206400	-1.88021600	H	1.36308800	-3.05891400	-0.26280400
C	2.29789900	-0.68893600	-2.45525600	H	1.33885800	-0.63766100	-2.97818800
H	2.66984800	0.33457200	-2.36243500	H	2.99877800	-1.26982100	-3.08242700
H	3.81659700	-0.27900800	-0.55381700	C	4.34870800	-2.35180700	-0.67141800
H	3.89623300	-3.33214700	-0.47217700	H	4.55532600	-2.31747500	-1.74807000
C	5.65545400	-2.25594400	0.12360700	C	5.36230500	-2.29564300	1.62573000
C	4.38598900	-1.17694600	2.00851800	H	4.87941600	-0.21256300	1.82681200
H	4.17344400	-1.21901500	3.08291200	H	6.28817400	-2.19819200	2.20671300
H	4.93023200	-3.27294500	1.88714000	H	6.32917600	-3.07311800	-0.16375600
H	6.17655300	-1.31889600	-0.12312300	H	2.56277300	-2.18215900	1.46516000
C	2.57145800	1.19632000	1.45472500	H	2.85749000	1.38609600	0.41636800
H	1.76216100	1.88461400	1.71119500	H	3.43110900	1.43486000	2.10441400
C	1.57372700	-0.36668700	2.97308800	H	0.74767600	0.33071900	3.14031700
H	1.19090500	-1.38466700	3.09101000	H	2.32997700	-0.18678500	3.75740000

Table A.2.42. 35 at –78 °C.



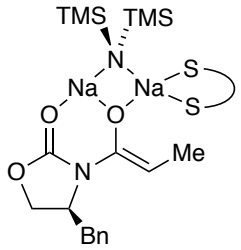


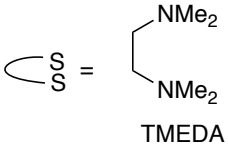
G = –1976.902878

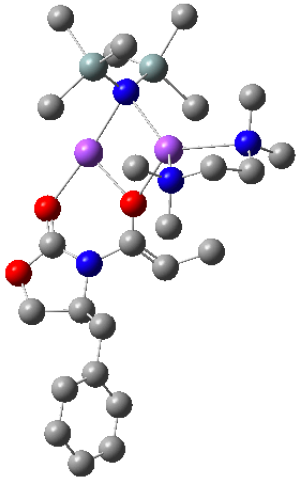
G_{MP2} = –1976.460738

C	0.00000000	0.00000000	0.00000000	O	-1.19301100	0.43280400	0.67945400
C	-2.27134700	0.17576900	-0.11196000	O	-3.40763200	0.29462700	0.33442500
Na	-5.22947500	0.70310900	-0.84648500	N	-7.11941000	0.94599800	-2.26424700
Si	-8.08679800	-0.42591800	-1.97071400	C	-9.95895100	-0.14887500	-1.79604300
H	-10.4808410	-1.09885200	-1.62295000	H	-10.1917110	0.51285200	-0.95259400
H	-10.3884300	0.30632500	-2.69627900	C	-7.85445000	-1.70854500	-3.37933900
H	-8.45183700	-2.61495800	-3.21680400	H	-8.16116900	-1.29248300	-4.35029500
H	-6.80853400	-2.04506800	-3.46575500	C	-7.51835900	-1.32706600	-0.38026700
H	-6.47198500	-1.66482500	-0.43535200	H	-7.61848900	-0.68158900	0.50414800
H	-8.11970800	-2.22528300	-0.18954800	Si	-7.36304000	2.61169900	-2.52534100
C	-6.61806200	3.65649300	-1.10784300	H	-6.73592200	4.73374600	-1.28268400
H	-7.10728000	3.42537500	-0.15172600	H	-5.53876400	3.47906900	-0.98171700
C	-6.40877600	3.15340300	-4.10413200	H	-5.32540600	2.97163300	-4.02159400
H	-6.78217800	2.63262500	-5.00021700	H	-6.52140500	4.22718300	-4.30100100
C	-9.15396800	3.20288400	-2.76309400	H	-9.63374500	2.70543300	-3.61514100
H	-9.76803200	2.99844600	-1.87821700	H	-9.18934400	4.28426900	-2.94821200
Na	-5.54637300	0.34333400	-3.85622200	O	-3.82475500	0.26582100	-2.53977300
C	-2.73614500	-0.43847600	-2.49998100	N	-1.85887700	-0.20651700	-1.35468000
C	-0.40100900	-0.08008700	-1.48285400	H	0.02132700	-0.97698000	-1.94217800
C	-0.00355700	1.15693000	-2.32112800	H	-0.54093100	1.08529800	-3.27358500
H	-0.36380200	2.05765100	-1.80906000	C	1.48712800	1.24596600	-2.56333900
C	2.28392600	2.16209600	-1.86383300	C	3.66374600	2.21943200	-2.07207200
C	4.26966900	1.35702900	-2.98587600	C	3.48700000	0.44091700	-3.69295700
C	2.10947100	0.38798200	-3.48302900	H	1.50454700	-0.31963300	-4.04655900
H	3.94958700	-0.22885900	-4.41323200	H	5.34275000	1.40106600	-3.15112500
H	4.26264900	2.94113500	-1.52281100	H	1.81708100	2.84628000	-1.15833100
C	-2.32031900	-1.32890300	-3.43805400	H	-1.42373000	-1.91736300	-3.28061200
C	-3.11470400	-1.55944500	-4.69417000	H	-2.57962900	-2.21276100	-5.39148000
H	-4.09071000	-2.04300400	-4.50733000	H	-3.31424600	-0.61956900	-5.24000100
H	0.79328200	0.72262700	0.19814500	H	0.29081400	-0.97660400	0.40246800

Table A.2.43. 36a at –78 °C.





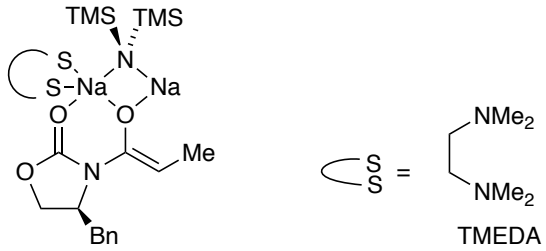


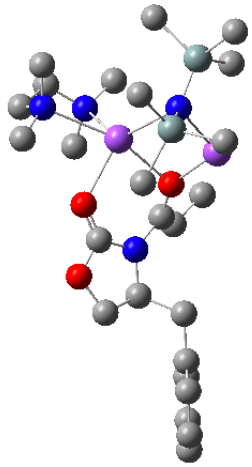
G = –2323.446494
G_{MP2} = –2322.783861

C	0.00000000	0.00000000	0.00000000	O	-1.11496100	-0.89757800	-0.13669500
C	-2.19253700	-0.20350400	-0.59377200	O	-3.28536200	-0.75090300	-0.69551800
Na	-5.19795900	0.36062700	-0.59408500	N	-7.23055900	1.46251300	-0.24165900
Si	-8.21548500	1.30541300	-1.63504000	C	-9.94826600	2.09542700	-1.49931600
H	-10.5068260	2.01527600	-2.44116700	H	-10.5508170	1.61217800	-0.71992000
H	-9.88448400	3.16119000	-1.24226300	C	-7.35907200	2.14676900	-3.12244400
H	-7.90572900	1.95812000	-4.05542900	H	-7.30690200	3.23715600	-2.99790900
H	-6.33081900	1.78783600	-3.26741800	C	-8.48995500	-0.50789900	-2.16986900
H	-7.53665400	-1.01401700	-2.38223900	H	-8.99593800	-1.08436000	-1.38582100
H	-9.10039400	-0.57761500	-3.07995200	Si	-7.69411100	1.15991000	1.37748400
C	-8.97146600	-0.23060300	1.65146600	H	-9.17087200	-0.37865500	2.72111900
H	-9.93155800	-0.01108200	1.16793800	H	-8.61466800	-1.18710700	1.24821000
C	-6.14913600	0.63012000	2.38129500	H	-5.79485200	-0.36786500	2.08080300
H	-5.30932800	1.32873800	2.25803400	H	-6.36376700	0.57055800	3.45617000
C	-8.40736100	2.70504400	2.24760900	H	-7.71371000	3.55447500	2.18122500
H	-9.34650300	3.01479800	1.77115600	H	-8.61532700	2.52942900	3.31128700
Na	-5.71454800	3.35332600	-0.42932400	O	-3.91956600	2.14407500	-0.97052500
C	-2.76160300	2.03357000	-1.54137100	N	-1.84171000	1.08021900	-0.89174000
C	-0.38561400	1.24905000	-0.81467400	H	0.05100700	1.19127400	-1.82176700
C	0.04752200	2.57212300	-0.16000600	H	-0.41220700	3.38707600	-0.72961000
H	-0.36764800	2.60909100	0.85468500	C	1.55262500	2.73375700	-0.11820100
C	2.26778900	3.04997600	-1.28343600	C	3.65628800	3.17769400	-1.25956700
C	4.35739700	2.99376900	-0.06552600	C	3.65892900	2.68397000	1.10172700
C	2.26875300	2.55531300	1.07291000	H	1.73142300	2.32368900	1.99017200
H	4.19413600	2.54539600	2.03749400	H	5.43896500	3.09636500	-0.04517800

H	4.19090600	3.42684200	-2.17248800	H	1.72884300	3.20704200	-2.21547100
C	-2.28424300	2.69359400	-2.62925300	H	-1.29467600	2.44993300	-3.00451200
C	-3.07296100	3.72411100	-3.38614700	H	-3.04567300	3.53891900	-4.46886600
H	-4.12460900	3.71009300	-3.08228300	H	-2.69464100	4.75023700	-3.23952600
N	-4.65949600	4.88732000	1.33905100	C	-4.72535500	4.46944100	2.74401300
H	-4.29506500	3.46940200	2.84964800	H	-4.17261300	5.15612000	3.41130400
H	-5.76688100	4.42879500	3.07534200	C	-3.25979600	4.87350900	0.89164400
H	-2.63801500	5.58765800	1.46306100	H	-2.85649300	3.86616800	1.01410500
H	-3.18648800	5.11673000	-0.17080200	C	-5.27407200	6.21376200	1.18079900
H	-4.65739800	6.99598300	1.66470000	H	-6.22965700	6.20182300	1.71595900
C	-5.50084900	6.63958500	-0.27237200	N	-6.38921100	5.75555500	-1.04661600
C	-7.78229400	5.84996500	-0.58806900	H	-8.17317300	6.88191100	-0.65708900
H	-8.41069400	5.19989000	-1.20317500	H	-7.87485600	5.51258000	0.44733000
C	-6.31312800	6.11189800	-2.46983200	H	-6.96595100	5.45434800	-3.05044500
H	-6.62228800	7.15669200	-2.65502000	H	-5.28861300	5.98172600	-2.83036900
H	-5.89390000	7.67437300	-0.26132600	H	-4.54088600	6.68036700	-0.79690500
H	0.12779700	0.23282000	1.06388500	H	0.89649100	-0.50224400	-0.36627400

Table A.2.44. 36b at –78 °C.



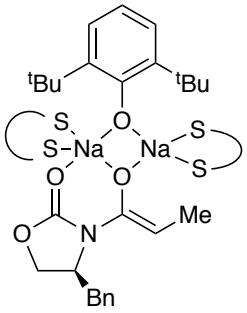


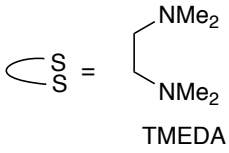
G = –2323.434659
G_{MP2} = –2322.772086

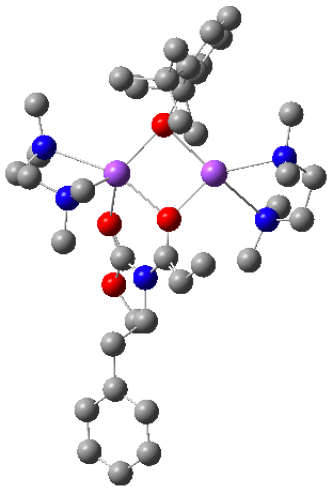
Na	0.00000000	0.00000000	0.00000000	O	1.88918300	0.68818900	-1.18477100
C	3.05625100	0.36497600	-1.00913600	O	3.96038200	0.44534600	-2.02618600
C	5.21664200	-0.09933900	-1.58696400	C	5.11674100	-0.16630400	-0.05006400

N	3.66369300	-0.08018300	0.12831300	C	2.97015000	-0.15741000	1.42009100
C	3.60929700	0.36345100	2.50049800	H	4.56021800	0.86984600	2.36015500
C	3.06369100	0.28519100	3.89854000	H	2.91861500	1.27982400	4.34588700
H	2.09147600	-0.21881100	3.90354100	H	3.73041700	-0.26476400	4.58070700
O	1.81545600	-0.74504600	1.37542300	Na	0.66184900	-2.46832600	1.75537200
N	-1.16868000	-2.26383500	0.42233500	Si	-2.45337200	-2.26409600	1.54913800
C	-3.50425900	-3.85338400	1.64578300	H	-4.29226200	-3.76239600	2.40500300
H	-3.99591400	-4.07506200	0.69042800	H	-2.89389800	-4.72715100	1.90775800
C	-1.72417500	-2.04612000	3.31877600	H	-2.51851100	-1.92812700	4.06679300
H	-1.14252500	-2.92776900	3.63788600	H	-1.07935700	-1.15860700	3.40469000
C	-3.69095400	-0.83095800	1.32751900	H	-3.18257700	0.14158800	1.34132700
H	-4.21010500	-0.91367600	0.36461000	H	-4.45342000	-0.81982200	2.11737600
Si	-1.02596700	-3.18990400	-1.01242000	C	-2.50825700	-3.07913300	-2.20805500
H	-2.34360000	-3.68119900	-3.11133600	H	-3.43582100	-3.43440200	-1.74171600
H	-2.68170100	-2.04425400	-2.52991600	C	0.51063500	-2.63153000	-1.99815600
H	0.43567700	-1.59840900	-2.36092500	H	1.42551800	-2.68885800	-1.39149800
H	0.66248000	-3.27180200	-2.87716300	C	-0.74285500	-5.05424200	-0.68484300
H	0.16307100	-5.22198300	-0.08236500	H	-1.58253200	-5.50321600	-0.14079200
H	-0.61452300	-5.61727600	-1.61882900	H	5.60301800	0.71140000	0.39917400
C	5.73633300	-1.43986300	0.55301700	H	5.47636000	-1.46199200	1.61686800
H	5.26294800	-2.31093500	0.08351000	C	7.23873500	-1.49291700	0.37122600
C	8.07986900	-0.69963400	1.16642100	C	9.46277200	-0.71873200	0.98749800
C	10.0320680	-1.53625700	0.00844700	C	9.20847200	-2.33489300	-0.78548100
C	7.82413100	-2.31174300	-0.60375900	H	7.19041600	-2.94615100	-1.21987200
H	9.64202100	-2.98065100	-1.54463400	H	11.1097460	-1.55461100	-0.12954300
H	10.0970530	-0.09991300	1.61687400	H	7.64567600	-0.06930600	1.93973400
H	5.33513000	-1.09513100	-2.02961100	H	6.01895400	0.54779100	-1.94471600
N	-1.37969400	1.48014000	-1.71592100	C	-1.08212600	2.83841800	-1.23349400
C	-1.31859800	3.03592300	0.26818000	N	-0.38059700	2.29078000	1.12219600
C	-0.88642600	2.19897900	2.49473200	H	-1.86031400	1.69954500	2.50396600
H	-0.18918800	1.60778700	3.09639800	H	-1.00047400	3.19033400	2.97213200
C	0.94859000	2.91704500	1.13338900	H	1.62815800	2.32262200	1.74991700
H	1.36584500	2.94246100	0.12520300	H	0.90936600	3.94850100	1.53204400
H	-1.27173600	4.12044900	0.48624400	H	-2.33332400	2.71415400	0.52479100
H	-1.68624800	3.58898600	-1.77964300	H	-0.03513000	3.04973400	-1.46977300
C	-2.82420000	1.24486300	-1.79400600	H	-3.00888200	0.22058400	-2.12874300
H	-3.29172500	1.35821500	-0.81359600	H	-3.31935100	1.93862400	-2.50003100
C	-0.77464500	1.26892600	-3.03790400	H	0.31127400	1.35880200	-2.96236200
H	-1.01218600	0.25888500	-3.38683500	H	-1.15144100	1.98790700	-3.78947900

Table A.2.45. **7** at –78 °C.





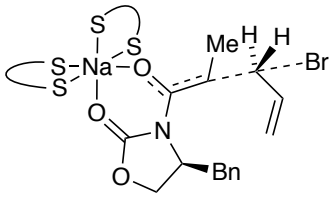


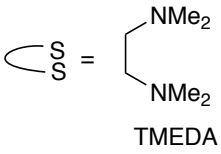
G = –2418.055192
G_{MP2} = –2417.079886

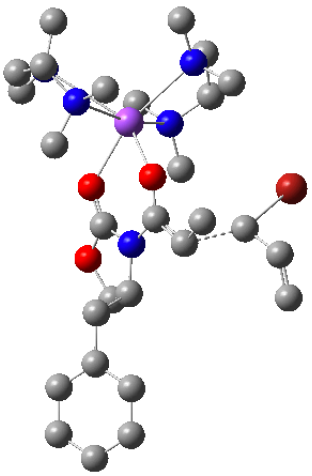
Na	0.00000000	0.00000000	0.00000000	O	-1.76405900	0.37731300	1.46863700
C	-2.75824200	1.06313300	1.28481200	O	-3.72919600	1.13464600	2.25038600
C	-4.69781300	2.12324000	1.85623000	C	-4.54844500	2.19396400	0.33193200
N	-3.13907200	1.80482600	0.19794600	C	-2.26970100	2.15654900	-0.93368900
C	-2.86523000	2.67870000	-2.04671100	H	-3.94098400	2.80081200	-2.09227900
C	-2.07310300	3.09833200	-3.25349800	H	-2.48291100	2.67347400	-4.18151600
H	-2.05611500	4.19157900	-3.40157300	H	-1.03575200	2.76073200	-3.16449600
O	-1.01179600	1.95906500	-0.73638300	Na	0.80052400	3.13248000	-0.20882000
N	1.91852900	5.13653800	-1.34711300	C	3.38185200	4.99240600	-1.28222200
H	3.70250200	4.89632000	-0.24127600	H	3.68852900	4.08124100	-1.79960000
H	3.90326800	5.85371000	-1.73827100	C	1.48638700	5.17744800	-2.75029900
H	0.39701000	5.23874100	-2.81984700	H	1.92004900	6.03974900	-3.29001900
H	1.80015200	4.26087100	-3.25590100	C	1.49414000	6.35083700	-0.63025900
H	1.70867700	7.25425500	-1.23199200	H	2.10406300	6.43237400	0.27501700
C	0.01095900	6.35740200	-0.25083400	N	-0.33293300	5.37439500	0.78927900
C	0.09522600	5.83270900	2.11504500	H	-0.14032200	5.06808700	2.86034400
H	1.17504100	5.99972200	2.14026100	H	-0.40695800	6.77403200	2.40735800
C	-1.77986600	5.13126500	0.80619700	H	-2.00891400	4.37859200	1.56670700
H	-2.35440300	6.04737200	1.04063500	H	-2.10878700	4.74258000	-0.16171100
H	-0.26786900	7.38080400	0.06577900	H	-0.59408300	6.13175500	-1.13493300
O	1.94391600	1.12734800	0.06847000	C	3.22840600	1.42484400	0.10551800
C	3.83559200	1.91841100	1.32071600	C	5.14647900	2.40704800	1.27448800
C	5.90913900	2.37644700	0.10973700	C	5.37350700	1.77678800	-1.02715800

C	4.06688500	1.27655400	-1.06326400	C	3.56717900	0.51705100	-2.31486900
C	3.19754700	-0.92874900	-1.90595900	H	2.43948700	-0.92465200	-1.12062900
H	2.81786900	-1.49270800	-2.76967300	H	4.08091200	-1.45456800	-1.52421600
C	4.64681700	0.40663400	-3.41311000	H	5.54400900	-0.11269100	-3.05862200
H	4.24655900	-0.16556800	-4.25888500	H	4.94987200	1.38825200	-3.79610100
C	2.34373000	1.20371800	-2.96538600	H	1.50900700	1.28438600	-2.26760300
H	2.61217400	2.21006000	-3.31072500	H	2.00827000	0.63802700	-3.84535000
H	6.00352300	1.69763800	-1.90658400	H	6.92314500	2.76788300	0.10273400
H	5.60191300	2.81291400	2.17157800	C	3.09381800	1.82133300	2.67581000
C	2.79310000	0.33290500	2.97381200	H	2.21770200	-0.10487800	2.15508800
H	3.72559500	-0.23270700	3.08653800	H	2.21800700	0.23041800	3.90454400
C	3.93796700	2.36157700	3.85007500	H	4.88819000	1.82721800	3.95477300
H	4.15904700	3.43082400	3.74321700	H	3.38258100	2.23202200	4.78672600
C	1.76453600	2.61260500	2.68730200	H	1.01702400	2.13751600	2.04965400
H	1.35196700	2.65756500	3.70419200	H	1.92850800	3.64509400	2.35395300
H	-4.68701000	3.21234600	-0.03964500	C	-5.50777000	1.22331300	-0.40573400
H	-5.16785800	1.13200500	-1.44205700	H	-5.40824800	0.23135300	0.05203100
C	-6.95165600	1.67474200	-0.36018900	C	-7.88703000	1.03577100	0.46485900
C	-9.21251900	1.47208900	0.52193900	C	-9.62483600	2.55962200	-0.24822700
C	-8.70443900	3.20433000	-1.07808400	C	-7.38237400	2.76434200	-1.13284500
H	-6.67635200	3.26658000	-1.79127200	H	-9.01822000	4.04757300	-1.68791600
H	-10.6559850	2.89992500	-0.20721000	H	-9.92199600	0.95865600	1.16562100
H	-7.57631900	0.17990500	1.06060300	H	-5.68380100	1.79253700	2.18629800
H	-4.44942800	3.07455200	2.34186000	N	-1.09532900	-1.64358100	-1.67037100
C	-0.74114300	-3.00131000	-1.23163400	H	0.27350700	-3.21036400	-1.58566500
H	-1.40007700	-3.75389100	-1.70729700	C	-0.80390100	-3.19898600	0.28686500
H	-1.78554500	-2.88601000	0.65638700	H	-0.72265800	-4.28318900	0.49839200
N	0.21347800	-2.44351500	1.03327900	C	1.53615300	-3.06518100	0.91383500
H	2.27379000	-2.45903400	1.44638300	H	1.55202100	-4.08856300	1.33480100
H	1.84678000	-3.11912800	-0.13234200	C	-0.16300000	-2.34917100	2.44994000
H	0.60670800	-1.79322400	2.99257200	H	-1.10385500	-1.80206900	2.54339500
H	-0.26760000	-3.34466100	2.92116000	C	-2.53823200	-1.40013900	-1.57014800
H	-2.86820200	-1.47902100	-0.53150600	H	-2.75891300	-0.38659200	-1.91620700
H	-3.12033600	-2.11761100	-2.17977200	C	-0.65518800	-1.41080300	-3.04925100
H	-0.88131100	-0.37821700	-3.33072600	H	0.42593300	-1.55703000	-3.12350100
H	-1.15092100	-2.08720600	-3.77094300				

Table A.2.46. **4a** reacting with allyl bromide from favored face at –78 °C.







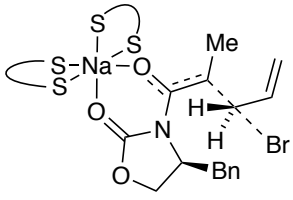
G = –4323.694916

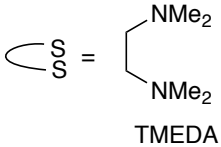
G_{MP2} = –4322.963364

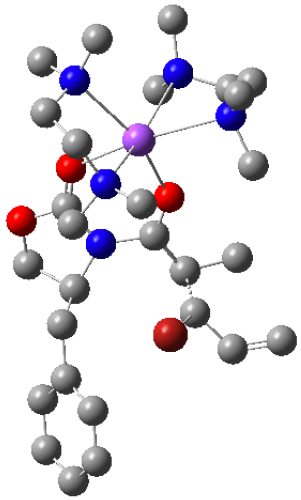
Na	0.00000000	0.00000000	0.00000000	O	1.86983900	0.55007600	1.19894700
C	3.10307500	0.68316500	1.00354200	N	3.65370200	0.13111600	-0.22705300
C	2.93822900	-0.59040300	-1.16124000	O	3.75405000	-0.90204300	-2.21157500
C	4.99607200	-0.18823400	-2.07051200	H	5.80350900	-0.82159200	-2.44037100
H	4.94327400	0.72723500	-2.67042200	C	5.08556400	0.10709700	-0.56903700
H	5.53220900	1.08806800	-0.39454000	C	5.85416700	-0.97834100	0.22460000
H	5.66226000	-0.81286900	1.29016600	H	5.42679100	-1.95595200	-0.03070400
C	7.34186200	-0.96817300	-0.05348200	C	7.93558700	-1.94937300	-0.85867600
C	9.30439100	-1.92108200	-1.13440600	C	10.1030930	-0.90604500	-0.60753900
C	9.52536300	0.07683500	0.19968800	C	8.15844500	0.04407800	0.47357400
H	7.72091600	0.80888700	1.11231000	H	10.1409300	0.86740400	0.62066000
H	11.1685390	-0.88237600	-0.81943000	H	9.74504100	-2.69470400	-1.75772200
H	7.32163700	-2.75098300	-1.26406500	O	1.77767500	-0.96140200	-1.15609000
C	3.96855800	1.43374400	1.81395400	H	5.03147400	1.44188000	1.60583700
C	3.56068000	1.77583700	3.22333800	H	2.49439000	2.01971800	3.27748200
H	3.73371000	0.94401300	3.92413900	H	4.12871400	2.63471300	3.59838200
N	-1.68924200	-2.43268000	-0.74723400	C	-1.33814000	-3.39844400	0.30441600
C	-1.28378600	-2.80906800	1.71605200	N	-0.19856200	-1.84339000	1.91706100
C	-0.35066900	-1.15365100	3.20124100	H	-0.25812500	-1.83955800	4.06481300
H	0.41797400	-0.38006800	3.27994100	H	-1.33521500	-0.67780900	3.25405100
C	1.11860900	-2.49005800	1.87501900	H	1.32233000	-2.88965900	0.87934900
H	1.87896300	-1.73757100	2.08514500	H	1.19839700	-3.30952400	2.61490100
H	-2.22922600	-2.30277000	1.94233400	H	-1.20262700	-3.65189200	2.43167800
H	-0.36255500	-3.82421600	0.05311400	H	-2.04994600	-4.24697200	0.31094100
C	-3.12814100	-2.16956300	-0.75989100	H	-3.45431200	-1.77658100	0.20728400

H	-3.36103700	-1.42020500	-1.52310400	H	-3.72326300	-3.07771600	-0.97732500
C	-1.25933400	-2.93958800	-2.05393300	H	-1.56643800	-2.24221100	-2.83778500
H	-0.16852300	-3.01681800	-2.07680900	H	-1.69534500	-3.92905800	-2.28881600
N	-0.41192500	1.53084000	-2.18123600	C	-1.16333100	0.66293900	-3.08698400
H	-1.46382200	1.18760700	-4.01457700	H	-0.54302900	-0.19500700	-3.36279500
H	-2.06898500	0.28663700	-2.60162900	C	0.82564700	1.96477400	-2.84520700
H	1.45748700	1.09133000	-3.03495200	H	0.62251400	2.46151300	-3.81251000
H	1.35617700	2.67856600	-2.20935300	C	-1.20606200	2.69853200	-1.76428500
H	-0.51514100	3.45507600	-1.38201800	H	-1.71730800	3.15714200	-2.63312900
C	-2.27621600	2.37944900	-0.71776400	H	-2.97138000	1.62774600	-1.11113100
H	-2.87255400	3.29746500	-0.55280400	N	-1.75605000	1.86375000	0.56199400
C	-2.87053400	1.37569600	1.37785200	H	-2.48915400	0.99538400	2.33029400
H	-3.60948400	2.16830400	1.60091700	H	-3.38878300	0.56115000	0.86081000
C	-1.03069000	2.90416800	1.30984900	H	-0.60104500	2.46338600	2.21524800
H	-0.21674300	3.33013600	0.71910800	H	-1.70152000	3.73139300	1.60750600
C	3.24579000	3.41025100	0.65360900	H	3.53653500	2.96749400	-0.28572000
H	2.33007000	3.08226800	1.10840900	C	4.12279400	4.37383800	1.30260800
H	3.73185200	4.84385300	2.20242300	C	5.34806600	4.70191200	0.86563300
H	5.76434200	4.27220700	-0.04307400	H	5.96341900	5.42785800	1.38822300
Br	1.75061800	4.98154900	-0.59495300				

Table A.2.47. **4a** reacting with allyl bromide from unfavored face at –78 °C.







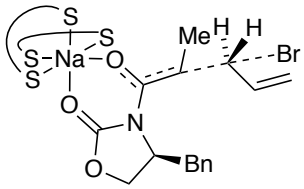
G = –4323.690428

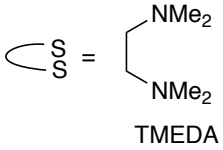
G_{MP2} = –4322.957114

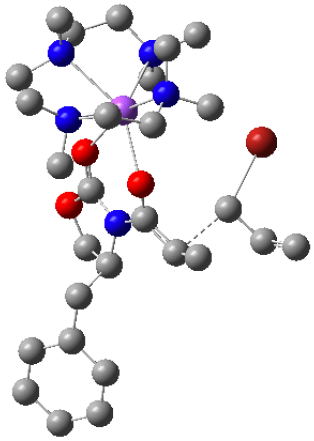
Na	0.00000000	0.00000000	0.00000000	O	1.70172400	0.20894500	-1.56082100
C	2.88196000	-0.19401300	-1.72890500	N	3.30453600	-1.32653900	-0.90793400
C	2.42301700	-2.16785900	-0.26222900	O	3.05821200	-3.33820700	0.04791800
C	4.33805800	-3.35345900	-0.61270900	H	5.03775300	-3.90241800	0.01913200
H	4.23007500	-3.86226300	-1.57826000	C	4.67291800	-1.86605500	-0.76824700
H	5.24753000	-1.68676500	-1.67676700	C	5.40785800	-1.28488100	0.47724600
H	4.92700400	-0.35174600	0.78023600	H	5.24828000	-1.97303100	1.31978400
C	6.89201400	-1.03589900	0.28637400	C	7.74431800	-2.02101700	-0.23412600
C	9.10808800	-1.77519500	-0.39717900	C	9.64437400	-0.53792800	-0.03540700
C	8.80682400	0.44749900	0.48882700	C	7.44120100	0.20298600	0.64899100
H	6.79460800	0.98060600	1.05343300	H	9.21308100	1.41388700	0.77576300
H	10.7066990	-0.34546800	-0.16041000	H	9.75159400	-2.55173500	-0.80299900
H	7.34679800	-2.99534300	-0.51241500	O	1.25618300	-2.00195900	0.04898900
C	3.81850400	0.37647300	-2.60486200	H	4.78175300	-0.10408500	-2.73741000
C	3.34944300	1.24036400	-3.74157600	H	4.06385200	2.04418200	-3.95993400
H	3.21984600	0.66151900	-4.66961700	H	2.38509600	1.70189800	-3.50917400
N	-1.14322100	2.29725900	-0.79601300	C	-1.88636700	2.00227600	-2.03373400
C	-1.33890500	0.82049900	-2.84017400	N	-1.52480400	-0.48892900	-2.19400700
C	-2.93242600	-0.88464500	-2.15601300	H	-3.38389500	-0.93392700	-3.16577900
H	-3.01883300	-1.87547400	-1.69973700	H	-3.52172900	-0.18786400	-1.55354900
C	-0.74798400	-1.51172000	-2.90533900	H	-0.85201300	-2.47199100	-2.39011500
H	-1.08402400	-1.63913800	-3.95191200	H	0.30558200	-1.22797100	-2.89540400
H	-0.26494100	0.94931100	-3.00004300	H	-1.82281800	0.83653100	-3.83717900
H	-2.92810300	1.80785900	-1.75962400	H	-1.90546300	2.89010500	-2.69375200
C	-1.98838700	3.06604000	0.12222300	H	-1.43064900	3.28874500	1.03619000
H	-2.32438500	4.02627400	-0.31199500	H	-2.87507200	2.48300200	0.39266100
C	0.08599200	3.05139500	-1.08342200	H	0.61228600	3.26080500	-0.14725500
H	0.75318300	2.45778000	-1.71085700	H	-0.13013600	4.01337800	-1.58515600
N	0.79136300	0.79470400	2.54039600	C	-0.28051600	0.25322700	3.38811900
C	-0.77645000	-1.14020500	2.99414500	N	-1.53984800	-1.19088800	1.73492800
C	-2.85924200	-0.57145000	1.88004100	H	-2.76399200	0.48769700	2.13256400
H	-3.39982700	-0.64229800	0.93149900	H	-3.46936300	-1.06101600	2.66288000
C	-1.69261700	-2.58882500	1.31189000	H	-2.26712700	-2.62728700	0.38138900
H	-0.70781700	-3.02144100	1.12374800	H	-2.22244200	-3.19839600	2.06759500
H	0.07741000	-1.81537900	2.88594800	H	-1.38695000	-1.53555200	3.82950800
H	-1.11528200	0.96244000	3.36581800	H	0.05178800	0.20462000	4.44392000
C	0.97384900	2.22251400	2.84294700	H	1.19071100	2.39449300	3.91362400
H	1.81325000	2.62080800	2.26661700	H	0.06189900	2.77449900	2.59110800
C	2.06288400	0.09196400	2.78150700	H	2.01691300	-0.92874000	2.39387400
H	2.87214600	0.63097800	2.28152700	H	2.30512200	0.04926300	3.86022900

C	4.42232200	2.01253200	-0.86798400	H	4.82449200	1.13160100	-0.42079100
H	3.35682600	2.17156900	-0.83457000	C	5.29378100	2.89683900	-1.61108200
C	4.87161800	3.96275000	-2.31279600	H	3.82220800	4.24479800	-2.34204800
H	5.56515000	4.60007300	-2.85333800	H	6.35526800	2.65781500	-1.58321000
Br	4.60519300	2.86715600	1.48930600				

Table A.2.48. **4b** reacting with allyl bromide from favored face at –78 °C







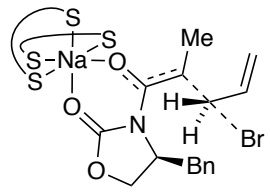
G = –4323.693275

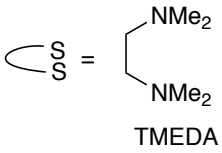
G_{MP2} = –4322.96188

Na	0.00000000	0.00000000	0.00000000	O	1.88180400	0.26768900	1.32894600
C	3.08540000	0.59138000	1.16877700	N	3.70620100	0.27023600	-0.10655300
C	5.15910600	0.23944100	-0.34603100	C	5.18085600	0.12163200	-1.87621500
O	3.91769300	-0.48344700	-2.20514900	C	3.03647300	-0.25851100	-1.19058800
O	1.85559100	-0.52272200	-1.32827500	H	5.98036300	-0.51813800	-2.25233900
H	5.23494100	1.10029600	-2.36573000	H	5.61890900	1.17967000	-0.03526200
C	5.83803000	-0.94605800	0.38145200	H	5.56577300	-0.88462000	1.44096100
H	5.41087900	-1.87880300	-0.00712400	C	7.34288900	-0.94878800	0.22196600
C	7.97829100	-1.83633000	-0.65671400	C	9.36488000	-1.81356200	-0.82194300
C	10.1393760	-0.89874700	-0.10825300	C	9.51974800	-0.01105700	0.77453800
C	8.13517000	-0.03819400	0.93753700	H	7.66308300	0.64872200	1.63728900
H	10.1160230	0.69950200	1.34080600	H	11.2184690	-0.88015600	-0.23396700
H	9.83816300	-2.51353500	-1.50542300	H	7.38231800	-2.56080200	-1.20791600
C	3.85557000	1.34756100	2.06950700	H	4.90394700	1.51630900	1.85169000
C	3.45586400	1.46508400	3.51149200	H	3.69369900	2.46220100	3.90600900
H	2.38286500	1.29261700	3.63546000	H	3.98193800	0.73647900	4.14721800
N	-1.36117900	0.40539200	2.17813700	C	-0.83642500	-0.40056300	3.29690800

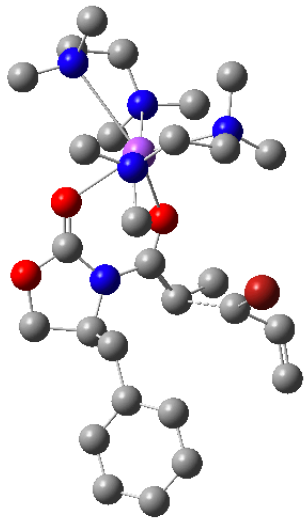
C	-1.18379200	-1.89268200	3.29454400	N	-0.65439800	-2.68002900	2.17767600
C	0.80273000	-2.81506700	2.24514600	H	1.14726200	-3.41988800	1.39933700
H	1.28677000	-1.83891500	2.17331500	H	1.13333000	-3.31315700	3.17855000
C	-1.27483700	-4.00316100	2.16592800	H	-2.36193600	-3.90898800	2.06726800
H	-0.90331400	-4.57890800	1.31162300	H	-1.06442000	-4.58540300	3.08458200
H	-0.82896500	-2.29869900	4.26460800	H	-2.27234900	-2.01578900	3.30051100
H	0.24887500	-0.26631300	3.30084000	H	-1.21464300	0.00220100	4.25795200
C	-2.81947400	0.32361200	2.07252200	H	-3.13011900	-0.68840500	1.80286500
H	-3.32838200	0.61125900	3.01217500	H	-3.16070000	1.00175400	1.28393800
C	-0.95965700	1.80492000	2.38773500	H	0.12992200	1.86008500	2.43973600
H	-1.29634300	2.42336200	1.55072300	H	-1.38118600	2.22428100	3.32030800
N	-1.30465000	-1.54794500	-1.57069100	C	-1.43364400	-0.76489100	-2.81032600
C	-1.96605700	0.65550500	-2.59920100	N	-1.05950500	1.54258200	-1.85474100
C	0.07861500	1.96544100	-2.69151900	H	0.71516100	1.11102400	-2.93268800
H	-0.26588500	2.43172700	-3.63344900	H	0.67021600	2.70225500	-2.14038300
C	-1.78982000	2.73759300	-1.40455100	H	-2.59471600	2.44479600	-0.72002800
H	-1.09956600	3.41101100	-0.88836800	H	-2.24324900	3.28937000	-2.24875800
H	-2.91692400	0.61602000	-2.05583500	H	-2.19899400	1.08325000	-3.59365100
H	-0.44322600	-0.71833700	-3.27247200	H	-2.09735700	-1.28018200	-3.53182800
C	-2.60750400	-1.94947900	-1.03637300	H	-2.45427800	-2.47506700	-0.09052100
H	-3.22951600	-1.07335900	-0.83667400	H	-3.15807200	-2.61263400	-1.73070800
C	-0.48106900	-2.73953200	-1.80368000	H	0.51197700	-2.43558500	-2.14204500
H	-0.37287100	-3.28903800	-0.86347400	H	-0.92883400	-3.41864300	-2.55352400
Br	1.35371500	4.76406000	-0.33473700	C	2.90348600	3.31270000	1.08367700
H	3.16525200	2.90606600	0.12465100	H	2.00183200	2.96374000	1.55703200
C	3.74498100	4.31313200	1.70984700	H	4.63642700	4.60567800	1.15720900
C	3.49443500	4.88332200	2.90085500	H	4.16148700	5.62759100	3.32556100
H	2.59296700	4.65525000	3.46316500				

Table A.2.49. **4b** reacting with allyl bromide from unfavored face at –78 °C.





TMEDA



G = –4323.690354

G_{MP2} = –4322.956688

Na	0.00000000	0.00000000	0.00000000	O	-1.63755200	-0.19857400	1.57089800
C	-2.73676900	-0.80026200	1.66902700	N	-3.05472800	-1.76129900	0.61192000
C	-4.39602300	-2.24475200	0.23412800	C	-4.01766200	-3.63348700	-0.29632800
O	-2.68714300	-3.44607900	-0.81424700	C	-2.10284600	-2.40170700	-0.14872200
O	-0.91457500	-2.16604700	-0.29370300	H	-4.65009000	-3.98486200	-1.11292100
H	-3.98322200	-4.38863100	0.49827000	H	-5.03882900	-2.32078700	1.11154800
C	-5.04895000	-1.33880600	-0.84942600	H	-4.61875600	-0.33683300	-0.78264600
H	-4.74676800	-1.71752600	-1.83678900	C	-6.56040200	-1.22875900	-0.77783300
C	-7.38372400	-2.35844300	-0.66075400	C	-8.77218500	-2.23084300	-0.60590400
C	-9.36293700	-0.96764500	-0.67254400	C	-8.55446800	0.16353300	-0.79260800
C	-7.16463700	0.03618000	-0.84460600	H	-6.54172800	0.92557300	-0.93007600
H	-9.00213100	1.15242300	-0.84637500	H	-10.4443300	-0.86734500	-0.63165800
H	-9.39207500	-3.11919900	-0.51449700	H	-6.94425800	-3.35280500	-0.61535800
C	-3.69448900	-0.57269700	2.66585500	H	-4.57925100	-1.20048700	2.70480900
C	-3.28021700	0.06806200	3.96542300	H	-4.13158900	0.55154500	4.45775900
H	-2.86961900	-0.66725200	4.67582700	H	-2.50546200	0.82399500	3.80191500
N	-0.68273100	0.62920000	-2.49680400	C	-0.22439900	2.00508300	-2.74457900
C	-0.58078300	2.99408700	-1.63323700	N	0.04572000	2.68538500	-0.33380700
C	1.46015100	3.06229400	-0.32539600	H	2.01108200	2.51917100	-1.09893400
H	1.60505600	4.14613700	-0.49663800	H	1.90374800	2.81086500	0.64358800
C	-0.66028200	3.39384700	0.74423600	H	-1.73320500	3.19891200	0.67261300
H	-0.29368000	3.04706500	1.71574400	H	-0.51086900	4.48806800	0.68638200
H	-1.66402900	3.01831400	-1.48583900	H	-0.29173500	4.00650700	-1.97528200
H	-0.64136400	2.39553300	-3.69326900	H	0.86342500	1.96934200	-2.87886700

C	-2.14453600	0.52020400	-2.60172200	H	-2.43703000	-0.51286100	-2.39252700
H	-2.65686400	1.17587600	-1.89375500	H	-2.49892500	0.77596400	-3.61818600
C	-0.07179600	-0.28710000	-3.46243000	H	1.01869800	-0.20902600	-3.41287700
H	-0.35671300	-1.31529600	-3.21966500	H	-0.38309400	-0.07289400	-4.50237300
N	2.67065800	-1.18538700	-0.68621300	C	3.19605400	-1.61691400	0.61779300
C	2.96800900	-0.61609400	1.75295100	N	1.55565200	-0.42081200	2.09683800
C	0.96609900	-1.62456100	2.69761200	H	0.94961600	-2.44694800	1.97914200
H	1.52026800	-1.94651700	3.59975900	H	-0.06855200	-1.40579000	2.96308700
C	1.40055200	0.70224300	3.02455000	H	1.83422100	1.60900500	2.58969800
H	0.33466700	0.87242300	3.19847700	H	1.89596900	0.52092200	3.99738800
H	3.38271300	0.35994800	1.47422800	H	3.54787700	-0.96201700	2.63226700
H	2.71685900	-2.56638000	0.87209200	H	4.28090800	-1.82865600	0.55385400
C	3.57704000	-0.23466100	-1.32983400	H	3.14436100	0.10811900	-2.27540400
H	3.72730300	0.64190100	-0.69299600	H	4.56973200	-0.67490800	-1.54598900
C	2.45821500	-2.35049000	-1.55120600	H	1.68086700	-2.98849900	-1.12199900
H	2.11591000	-2.02073600	-2.53539500	H	3.37976800	-2.94624500	-1.69232200
C	-4.43140000	1.43823700	1.44412400	H	-5.02175600	0.75416900	0.86554500
H	-3.36568500	1.46664800	1.31615800	C	-5.08605500	2.22705700	2.47107500
H	-4.46788200	2.95234700	2.99586400	C	-6.38241800	2.09988500	2.79799200
H	-6.83521500	2.70546100	3.57747500	H	-7.03065300	1.39452000	2.28327900
Br	-4.43688200	2.97237800	-0.54675300				

Chapter 2 References and Notes

1. (a) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835. (b) Wu, G.; Huang, M. *Chem. Rev.* **2006**, *106*, 2596. (c) Farina, V.; Reeves, J. T.; Senanayake, C. H.; Song, J. J. *Chem. Rev.* **2006**, *106*, 2734.

2. Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

3. (a) "Modern Aldol Reactions", Vols. 1 and 2 (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, 2004. (b) Lin, G.-Q.; Li, Y.-M.; Chan, A. S. C. *Principles and Applications of Asymmetric Synthesis*, Wiley & Sons: New York, **2001**; 135. (c) Mahrwald, R. in "Aldol Reactions", Springer, New York, 2009.

4. (a) Evans, D. A.; Takacs, J. M.; McGee, L. R.; Ennis, M. D.; Mathre, D. J.; Bartroli, J. *Pure Appl. Chem.* **1981**, *53*, 1109. (b) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737.

5. Tallmadge, E. H.; Collum, D. B. *J. Am. Chem. Soc.* **2015**, *137*, 13087.

6. Tallmadge, E. H.; Jermaks, J.; Collum, D. B. *J. Am. Chem. Soc.* **2016**, *138*, 345.

7. For an attempt to assemble a comprehensive bibliography of lithium-based Evans aldol additions, see ref 6.

8. Jermaks, J.; Tallmadge, E. H.; Keresztes, I.; Collum, D. B. *J. Am. Chem. Soc.* **2018**, *140*, 3077.

9. Zhang, Z.; Collum, D. B. *J. Org. Chem.* **2017**, *82*, 7595.

10. For other examples of physical studies of Evans enolates, see:
(a) Shinasha, C. B.; Sunoj, R. B. *J. Am. Chem. Soc.* **2010**, *132*, 12319. (b) Sreenithya, A.; Sunoj, R. B. *Org. Lett.* **2012**, *14*, 5752. (c) Shinisha, C. B.; Sunoj, R. B. *Org. Lett.* **2010**, *12*, 2868. (d) Goodman, J. M.; Paton, R. S. *J. Chem. Soc., Chem. Commun.* **2007**, 2124. (e) Baringhaus, K. H.; Matter, H.; Kurz, M. *J. Org. Chem.* **2000**, *65*, 5031. (f) Kimball, D. B.; Michalczyk, R.; Moody, E.; Ollivault-Shiflett, M.; De Jesus, K.; Silks, L. A. III *J. Am. Chem. Soc.* **2003**, *125*, 14666.

11. Tomasevich, L. L.; Collum, D. B. *J. Am. Chem. Soc.* **2014**, *136*, 9710.

12. For an interesting historical perspective on organoalkali metal chemistry, see: (a) Seyferth, D. *Organometallics* **2006**, *25*, 2. (b) Seyferth, D. *Organometallics* **2009**, *28*, 2.

13. Mulvey, R. E.; Robertson, S. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 11470.

14. Ma, Y.; Algera, R. F.; Collum, D. B. *J. Org. Chem.* **2016**, *81*, 11312.

15. Andrews, P. C.; Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A.; Barr, D.; Cowton, L.; Dawson, A. J.; Wakefield, B. J. *J. Organomet. Chem.* **1996**, *518*, 85.

16. "Sodium hexamethyldisilazide". Watson, B. T.; Lebel, H. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, New York; 2005, p 1–10.

17. (a) Ojeda-Amador, A. I.; Martinez-Martinez, A. J.; Kennedy, A. R.; Armstrong, D. R.; O'Hara, C. T. *Chem. Commun.* **2017**, *53*, 324. (b) Henderson, K. W.; Dorigo, A. E.; Liu, Q. Y.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 11855. (c) Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Robertson, S. D.; Robertson, G. M. *Acta Crystallographica, Section E: Structure Reports Online* **2012**, *68*, m1468.

18. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

19. Evans, D. A.; Britton, T. C.; Ellman, J. A. *Tetrahedron Lett*. **1987**, *28*, 6141.

20. We refer to $(LiX)_n$ and $(LiX)_m(LiX')_n$ as a "homoaggregate" and "heteroaggregate", respectively, and reserve the term "mixed aggregate" for $(LiX)_m(LiY)_n$.

21. Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 11998.

22. Job, P. *Ann. Chim.* **1928**, *9*, 113.

23. Houghton, M. J.; Collum, D. B. *J. Org. Chem.* **2016**, *81*, 11057.

24. Hibberta, D. B.; Thordarson, P. *Chem. Commun.* **2016**, *52*, 12792.

25. (a) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227. (b) Lucht, B. L.; Collum, D. B. *Acc. Chem. Res.* **1999**, *32*, 1035.

26. Algera, R. F.; Ma, Y.; Collum, D. B. *J. Am. Chem. Soc.* **2017**, *139*, 7921.

27. (a) Boyle, T. J.; Velazquez, A. T.; Yonemoto, D. T.; Alam, T. M.; Moore, C.; Rheingold, A. L. *Inorg. Chim. Acta* **2013**, *405*, 374. (b) Calvo, B.; Davidson, M. G.; Garcia-Vivo, D. *Inorg. Chem.* **2011**, *50*, 3589.

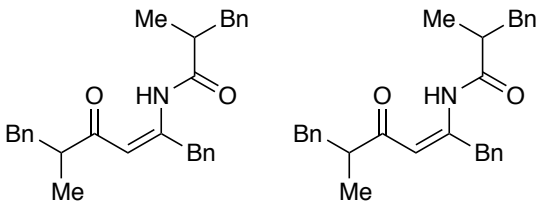
28. Collum, D. B.; McNeil, A. J.; Ramírez, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 3002.

29. Casado, J.; Lopez-Quintela, M. A.; Lorenzo-Barral, F. M. *J. Chem. Educ.* **1986**, *63*, 450.

30. We define the idealized rate law as that obtained by rounding the observed reaction orders to the nearest rational order.

31. For an excellent review of enolate quaterization including several examples involving oxazolidinones, see: Minko, Y.; Marek, I. *Chem. Commun.* **2014**, *50*, 12597.

32. The back bone metalation product was obtained at a roughly 50% yield and characterized by various ^{1}H and ^{13}C NMR correlation spectroscopies to be the structure below. It appears to derive from deprotonation of auxilliary oxygen-neighboring methylene proton followed by acylation at that position.



33. Schmidt, B.; Wildemann, H. *J. Chem. Soc., Perkin Trans. 1,* **2002**, 1050.

34. LiHMDS has been shown to be substantially more reactive in Et_3N/toluene than in THF solution: Zhao, P.; Collum, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 14411.

35. The oxazolidinone-NaHMDS complex in Et_3N/toluene shows IR absorbances at 1761 and 1711 cm^{-1}.

36. Addition of BF_3 to accelerate organolithium-based epoxide cleavages was first reported by Ganem and coworkers: Eis, M. J.; Wrobel, J. E.; Ganem, B. *J. Am. Chem. Soc.* **1984**, *106*, 3693.

37. Velazquez, F.; Olivo, H. *Current Org. Chem.* **2002**, *6*, 303.

38. Azaaldol additions using Evans enolates: (a) Bian, J.; Blakemore, D.; Warmus, J. S.; Sun, J.; Corbett, M.; Rose, C. R.; Bechle, B. M. *Org. Lett.* **2013**, *15*, 562. (b) Ma, Z.; Zhao, Y.; Jiang, N.; Jin, X.; Wang, J. *Tetrahedron Lett.* **2002**, *43*, 3209.

39. Azaaldols of alkali metal enolates to phenethylimines: Evans, C. D.; Mahon, M. F.; Andrews, P. C.; Muir, J.; Bull, S. D. *Org. Lett.* **2011**, *13*, 6276.

40. (a) Vemula, R.; Wilde, N. C.; Goreti, R.; Corey, E. J. *Org. Lett.* **2017**, *19*, 3883. (b) Díez, R.; Badorrey, R.; Díaz-de-Villegas, M. D.; Gálvez, J. A. *Eur. J. Org. Chem.* **2007**, *13*, 2114. (c) Kawate, T.; Yamada, H.; Yamaguchi, K.; Nishida, A.; Nakagawa, M. *Chem. Pharm. Bull.* **1996**, *44*, 1776.

41. Ma, Y.; Lobkovsky, E.; Collum, D. B. *J. Org. Chem.* **2005**, *70*, 2335.

42. The methyl stemming from the propionyl group appears as a broad 'singlet' in the ^1H NMR spectrum at room temperature. Raising the temperature causes considerable sharpening around 40 °C, affording the anticipated doublet at 60 °C. Lowering the temperature to –80 °C reveals two conformers attributed to hydrogen bonding. Despite the gamut of two-dimensional ^1H and ^{13}C NMR spectroscopies, the assignment was ultimately made by derivatizing **22** as the corresponding BOC-protected methyl ester and comparing it with an authentic sample: Seebach, D.; Abele, S.; Gademann, K.; Guichard, G.; Hintermann, T.; Jaun, B.; Mathews, J. L.; Schreiber, J. V. *Helv. Chim. Acta* **1998**, *81*, 932.

43. (a) Vemula, R.; Wilde, N. C.; Goreti, R.; Corey, E. J. *Org. Lett.* **2017**, *19*, 3883. (b) Veith, U.; Leurs, S.; Jäger, V. *Chem. Commun.* **1996**, *3*, 329. (c) Chandrasekhar, S.; Pendke, M.; Muththe, C.; Akondi, S. M.; Mainkar, P. S. *Tetrahedron Lett.* **2012**, *53*, 1292.

44. After several abortive attempts to ascertain the optical purity of **25** using HPLC and NMR shift reagents, reaction with the lithium salt of the oxazolidinone auxilliary afforded aldol adduct **23** contaminated by the other syn isomer (7:1) albeit in low (15%) yield.

45. (a) Gruver, J. M.; Liou, L. R.; McNeil, A. J.; Ramírez, A.; Collum, D. B. *J. Org. Chem.* **2008**, *73*, 7743. (b) Liou, L. R.; McNeil, A. J.; Ramírez, A.; Toombes, G. E. S.; Gruver, J. M.; Collum, D. B. *J. Am. Chem. Soc.* **2008**, *130*, 4859.

46. (a) Ashby, M. T.; Govindan, G. N.; Grafton, A. K. *Inorg. Chem.* **1993**, *32*, 3803. (b) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172. (c) Haq, I.; Lincoln, P.; Suh, D.; Norden, B.; Chowdhry, B. Z.; Chaires, J. B. *J. Am. Chem. Soc.* **1995**, *117*, 4788.

47. Bauer, W.; Schleyer, P. v. R. "Advances in Carbanion Chemistry"; Snieckus, V., ed.; JAI: New York, 1992, p 89.

48. (a) Edmonds, M. K.; Graichen, F. H. M.; Gardiner, J.; Abell, A. D. *Org. Lett.* **2008**, *10*, 885. (b) Peddie, V.; Pietsch, M.; Bromfield, K. M.; Pike, R. N.; Duggan, P. J.; Abell, A. D. *Synthesis* **2010**, *11*, 1845. (c) Falck, J. R.; Gao, S.; Prasad, R. N.; Koduru, S. R. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1768. (d) Minko, Y.; Marek, I. *Chem. Commun.* **2014**, *50*, 12597 and references cited therein.

49. Fuerstner, A.; Fenster, M. D. B.; Fasching, B.; Godbout, C. P.; Radkowski, K. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 5510.

50. Li, B.-J.; El-Nachef, C.; Beauchemin, A. M. *Chem. Commun.* **2017**, *53*, 13192.

51. (a) Koskinen, A. M. P.; Kataja, A. O. *Org. React.* **2015**, *86*, 105. (b) Mahrwald, R. in "Modern Aldol Reactions", Vol. 2 (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, 2004, pg 327.

52. Algera, R. F.; Ma, Y.; Collum, D. B. *J. Am. Chem. Soc.* **2017**, *139*, 15197.

53. (a) Ojeda-Amador, A. I.; Martinez-Martinez, A. J.; Kennedy, A. R.; O'Hara, C. T. *Inorg. Chem.* **2015**, *54*, 9833. (b) For a NaHMDS-sodium enolate mixed aggregate characterized crystallographically, see: Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 8602.

54. Mixed aggregation can tip the relative contributions of competing monomer- and dimer-based toward the monomer through the net dilution of the homoaggregates: Ramírez, A.; Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 10326.

55. For a discussion of aggregation and cooperative effects on the aldol addition, see: Larranaga, O.; de Cozar, A.; Bickelhaupt, F. M.; Zangi, R.; Cossio, F. P. *Chem. Eur. J.* **2013**, *19*, 13761.

56. Oxazolidinone precursors to enolates **2**, **9a-e**, and **10** were prepared according to literature procedures. (a) Mabe, P. J.; Zakarian, A. *Org. Lett.* **2014**, *16*, 516. (b) Kretschmer, M.; Dieckmann, M.; Li, P.; Rudolph, S.; Herkommer, D.; Troendlin, J.; Menche, D. *Chem. Euro. J.* **2013**, *19*, 15993. (c) Szostak, M.; Spain, M.; Eberhart, A. J.; Procter, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 2268. (d) Gille, A.; Hiersemann, M. *Org. Lett.* **2010**, *12*, 5258. (e) Bull, S. D.; Davies, S. G.; Jones, S.; Sanganee, H. J. *J. Chem. Soc., Perkin Trans.* **1999**, *4*, 387.

57. Kummer, D. A.; Chain, W. J.; Morales, M. R.; Quiroga, O.; Myers, A. G. *J. Am. Chem. Soc.* **2008**, *130*, 13231.

CHAPTER 3

WITTIG REARRANGEMENT OF BORON-BASED OXAZOLIDINONE ENOLATES

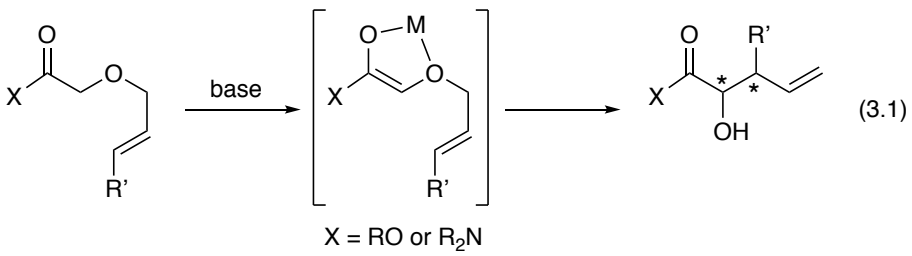
Wittig Rearrangements of Boron-Based Oxazolidinone Enolates

Abstract

[2,3]-Sigmatropic rearrangements (Wittig rearrangements) of a-alkoxy oxazolidinone enolates are described. Whereas alkali metal enolates fail owing to facile deacylation, boron enolates generated from di-*n*-butylboron triflate and triethylamine rearranged in good yields and high selectivities with exceptions noted. IR and NMR spectroscopies show the boron was chelated by the a-alkoxy group rather than the more distal oxazolidinone carbonyl in the complex and enolate. The rearrangement product contained a boron alkoxide that remained unchelated by either carbonyl. Optimization was guided by density functional theory computations suggesting that valine-derived oxazolidinones would be superior to the phenylalanine-derived analogs.

Introduction

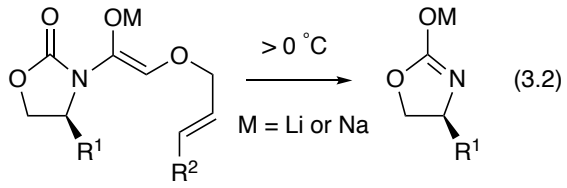
Wittig rearrangements of allyloxy-substituted enolates and related carbanions have enjoyed considerable popularity (eq 3.1).[1] Several aspects of this reaction captured our imagination. First, the aggregation of lithium enolates presents the possibility of rearranging *within an aggregate*, especially given mounting evidence that enolate aggregates equilibrate slowly on laboratory timescales.[2a] The consequences to stereochemistry would be considerable and pose some challenging but interesting questions. Second, our interest in the chemistry of oxazolidinone-derived Evans enolates[3] previously revealed that, while the lithium enolates in THF are highly aggregated,[2b] TMEDA-solvated sodium enolates are monomeric,[2c] raising the prospect of probing aggregation effects from two extremes. Lastly, there are no reports that describe the use of the Evans oxazolidinone auxiliaries for such [2,3]-sigmatropic rearrangements.[4]



(3.1)

Ultimately, the allure of employing sodium and lithium Evans enolates in the [2,3]-sigmatropic rearrangement proved for naught: both substrates failed to rearrange owing to competing deacylation pathways (eq 3.2).[2c] While this explained the absence of such rearrangements, it also brought into focus a more basic question: How *would* one carry out such a rearrangement?

After briefly exploring titanium enolates with little luck,[3] we were naturally drawn to boron enolates owing to reports of boron-based [2,3]-sigmatropic rearrangements on simpler systems,[5] boron-based aldol additions of Evans enolates including a-alkoxy cases,[3d,6] and our previous structural and mechanistic studies of the boron-based Evans enolates.[2d,7]



(3.2)

We describe herein structural, rate, and computational studies of the [2,3]-sigmatropic rearrangement outlined in eq 3.3. Although our interests are largely structural and mechanistic, we offer select examples that illustrate efficacy, applications, and logical steps toward optimization.

Results and Discussion

Methods. Emblematic results are illustrated in eq 3.3 and Table 3.1, with several more specialized examples discussed below (eqs 3.8–3.11). Dichloromethane (CH_2Cl_2) and $CDCl_3$ are used interchangeably. Substrates **1a**–**1f** were prepared from the alkoxy-substituted acids using standard protocols as described by eq 3.4.[8,9,10] The absolute and relative stereochemistries were determined by converting **2a** to triol **5**,[11] **2d** to lactone **6**,[12] and **2e** to lactone **7**.[12a] A quaternization (**23**, vide infra) was correlated with g-lactone **8**.[13] The stereochemistries of the remaining products were inferred by analogy. Stereocontrol in the rearrangement is discussed at greater length in a section below.

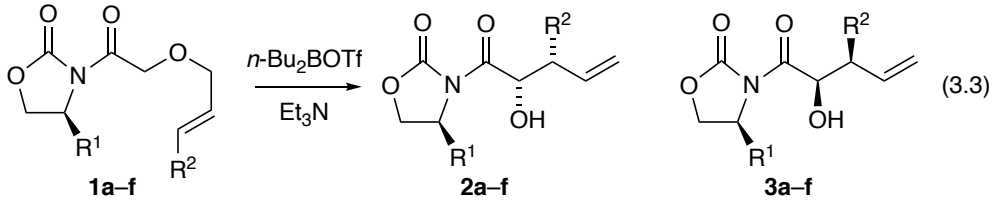
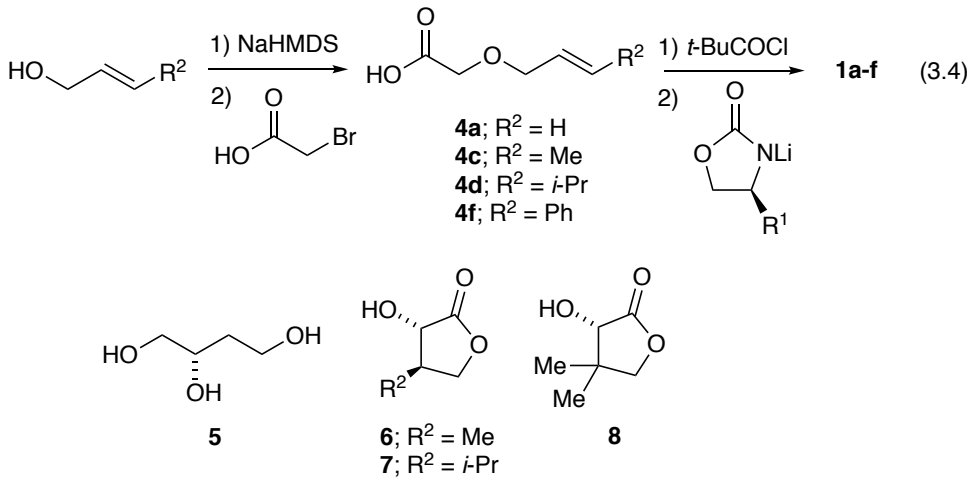


Table 3.1. [2,3]-Sigmatropic rearrangements of oxazolidinone-derived boron enolates.

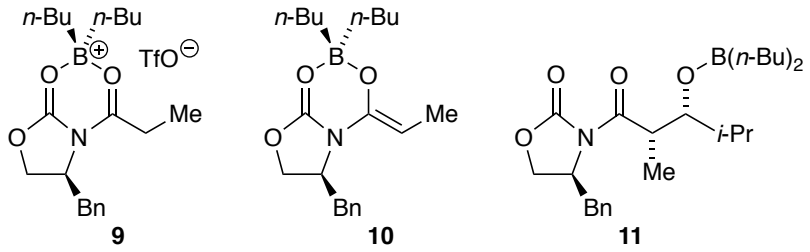
entry	substrate	R^1	R^2	temp	**2**:**3**	Yield
1	**1a**	Bn	H	0 °C to rt	2:1	90%
2	**1b**	*i*-Pr	H	0 °C to rt	3:1	81%
3	**1c**	Bn	Me	0 °C to rt	5:1	90%
4	**1d**	*i*-Pr	Me	0 °C to rt	>15:1[a]	82%
5	**1e**	*i*-Pr	*i*-Pr	0 °C to rt	>30:1	71%
6	**1f**	*i*-Pr	Ph	–78 °C to rt	>30:1	91%

[a]Starting substrate **1d** contains 6% cis isomer, which affords an anti isomer.



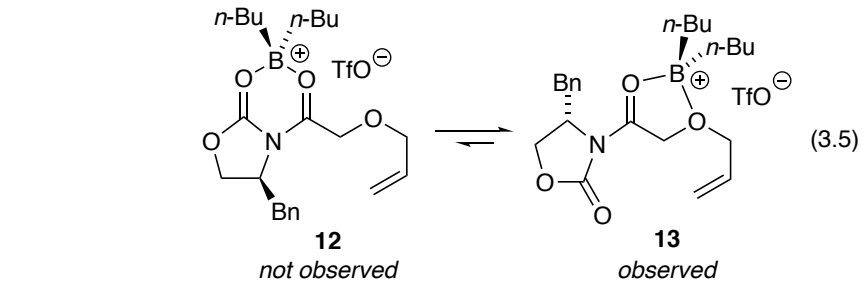
Previous studies showed that boron NMR spectroscopy would not be useful for studying oxazolidinone-derived intermediates **9**–**11**,[2d] whereas IR spectroscopy proved critical.[14] In the current study we again rely on IR spectroscopy and augment the

assignments with standard two-dimensional ^{1}H and ^{13}C NMR spectroscopies (COSY, HSQC, HMBC, and ROESY). Comparisons of key intermediates with propionate-derived species **9**–**11** reveal the relative importance of the alkoxy and oxazolidinone carbonyl as ligands for boron.



Density functional theory (DFT) calculations were carried out at the B3LYP/6–31G(d) level with single-point calculations at the MP2 level of theory.[15] Allusions to results without further elaboration are documented in the Supporting Information.

Oxazolidinone-Boron Complex. We first studied the [2,3] Wittig rearrangement of the simplest substrate, **1a**. IR spectroscopy showed that treatment of **1a** with 1.0–2.0 equiv of *n*-Bu_2BOTf at 0 °C causes oxazolidinone and carboxamide carbonyl absorbances of **1a** at 1783 cm^{-1} and 1719 cm^{-1} (Figure 3.1a) to be replaced by absorbances at 1825 cm^{-1} and 1613 cm^{-1}, respectively (Figure 3.1b). Given that the carboxamide and oxazolidinone carbonyls of propionate-derived complex **9** both appear at 1727 cm^{-1}, we conclude that complex **13**, with a complexed carboxamide and a relatively unperturbed oxazolidinone carbonyl, is formed to the exclusion of **12**, in which the oxazolidinone is complexed (eq 3.5). The full complement of 2D NMR spectroscopies show correlations, including those derived from the B-CH_2 and allyloxy O-CH_2 protons, that are consistent with the assignment of this intermediate as **13**. DFT computations show an 11.9 kcal/mol preference for **13**, which seems large but probably a consequence of the net charge. The computed structure of **13** shows a marked 180° rotation of the oxazolidinone moiety about the C-N bond relative to **12**.



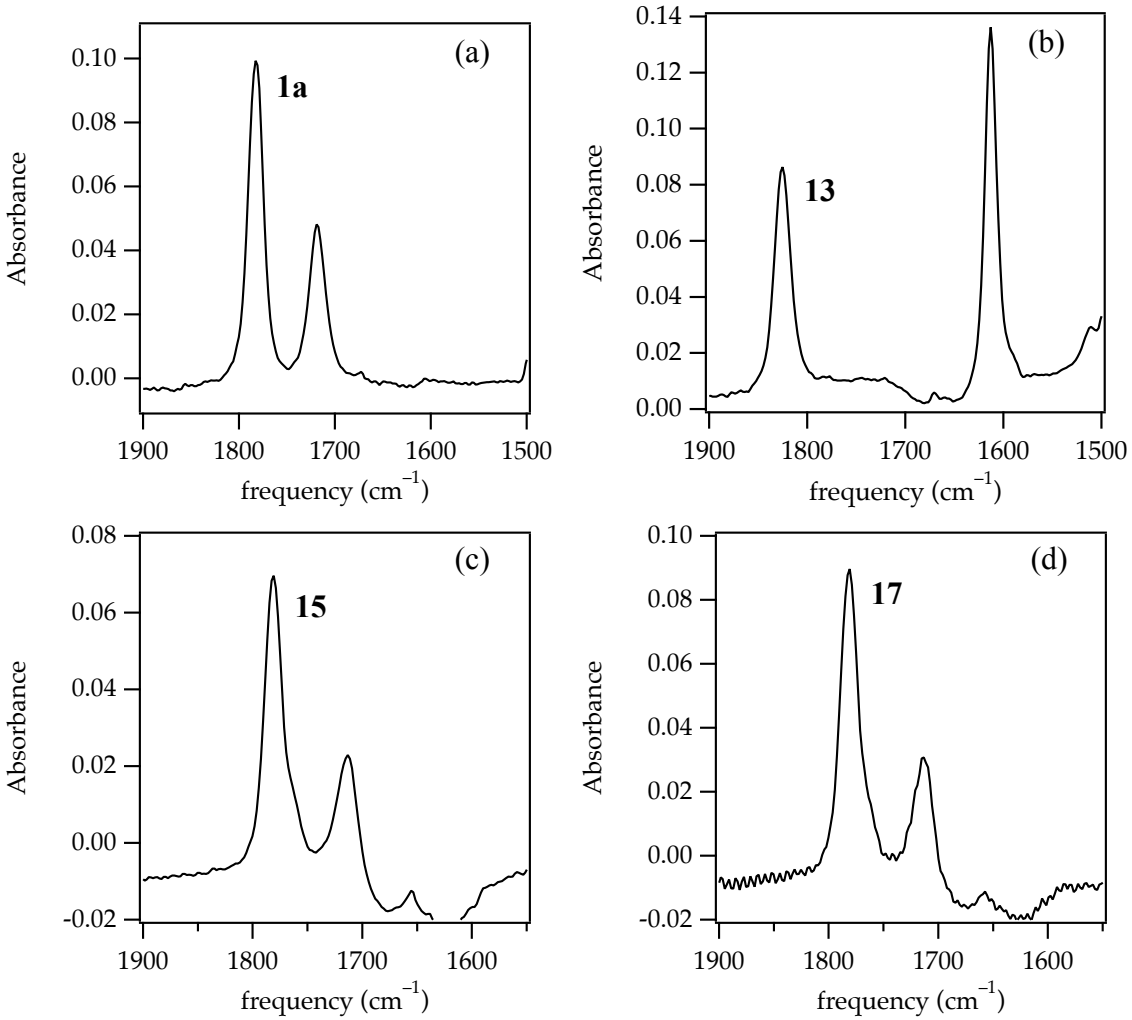
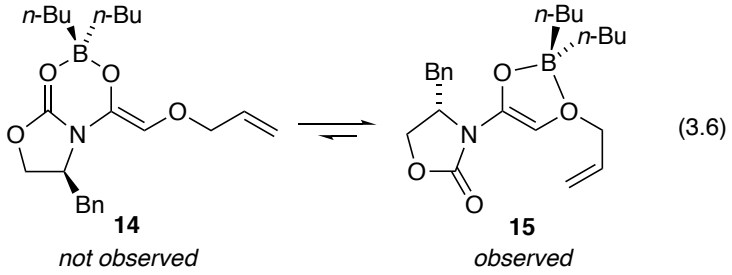


Figure 3.1. IR spectra of 0.030 M **1a** in CH_2Cl_2 recorded at 0 °C with (a) no additive, (b) 0.060 M *n*-Bu_2BOTf affording **13**, (c) 0.060 M *n*-Bu_2BOTf and 0.10 M Et_3N affording **15**, and (d) product **17** after warming to 25 °C.

Boron Enolate. Treatment of complex **13** with Et_3N at –30 °C causes immediate formation of boron enolate **15**, with absorbances for the oxazolidinone and enolate at 1781 cm^{-1} and 1713 cm^{-1}, respectively (Figure 3.1c). Once again, the minor shift of the oxazolidinone absorbance when compared with enolate **10** (1706 cm^{-1}) in the propionate series is consistent with ether-based chelate **15** and an uncomplexed oxazolidinone, rather than **14**. Two-dimensional NMR spectroscopies show a single *Z*-isomeric enolate **15**. DFT computations predict a 1.6 kcal/mol preference for **15** versus **14**.



(3.6)

Sigmatropic Rearrangement. Warming enolate **15** to 25 °C causes rearrangement following a clean, first-order decay (Figure 3.2) with formation of alkoxide **17** as a 2:1 mixture of diastereomers (confirmed after workup) in 90% isolated yield. The absorbances for **17** at 1779 cm^{-1} and 1711 cm^{-1}, respectively (Figure 3.1d), show that the boron alkoxide is not chelated by either carbonyl. DFT computations predict a 4.9 kcal/mol preference for open (unchelated) three-coordinate alkoxide **17** (analogous to **11)** relative to the chelate **16**.

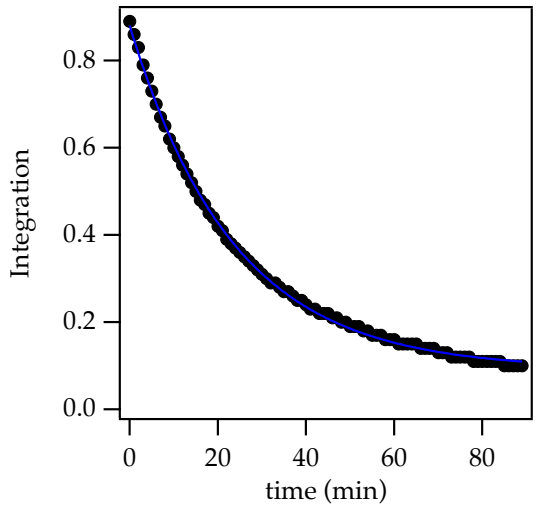
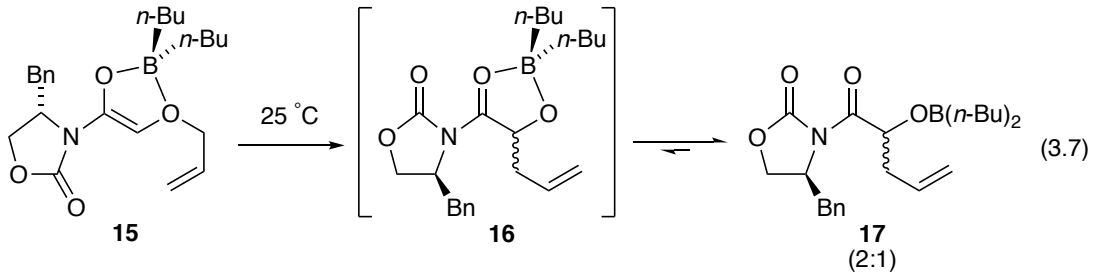


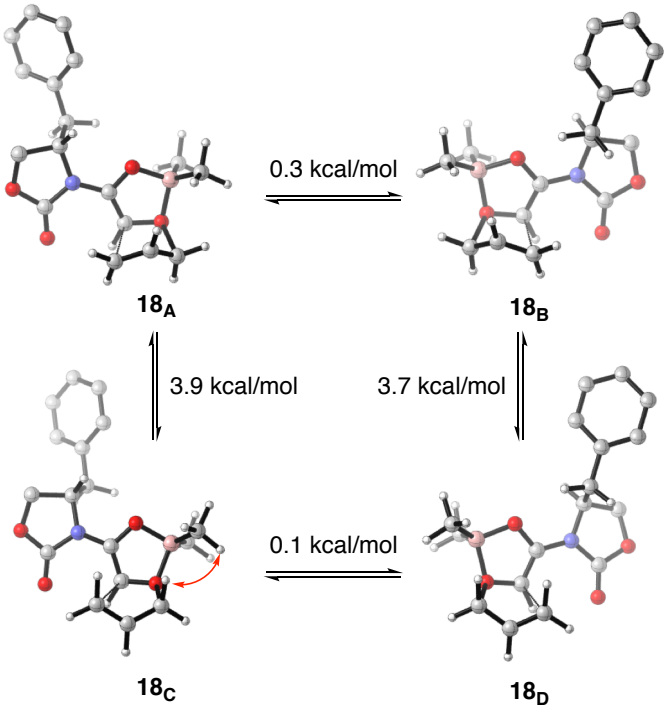
Figure 3.2. First-order decay of the rearrangement of enolate **15** to give alkoxide **17**.



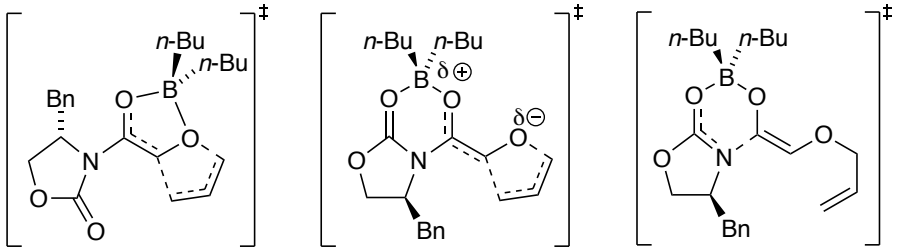
15 **16** **17** (2:1) (3.7)

The rearrangement in eq 3.7 represents the simplest mechanism we have ever studied. The first-order decay is operationally the entire rate law. The first-order rate constant is independent of initial concentration and unaffected by excess Et_3N. DFT computations were carried out on four isomeric transition structures **18** (Scheme 3.1). The benzyl moiety appears to not only be an inadequate stereochemical determinant in this simple case but seemed likely to remain so even with substituents placed on the allyloxy fragment. A significant preference for half-chair conformers $\mathbf{18_A}$ and $\mathbf{18_B}$ relative to $\mathbf{18_C}$ and $\mathbf{18_D}$ appears to derive from unfavorable OC*H*–*H*CB interactions (see arrow) in the latter two.

Scheme 3.1. DFT computed stereoisomers of transition structure **18** using methyls as surrogates for *n*-butyls for the rearrangement of **1a** to major and minor products **2a** and **3a** (Table 3.1, entry 1).



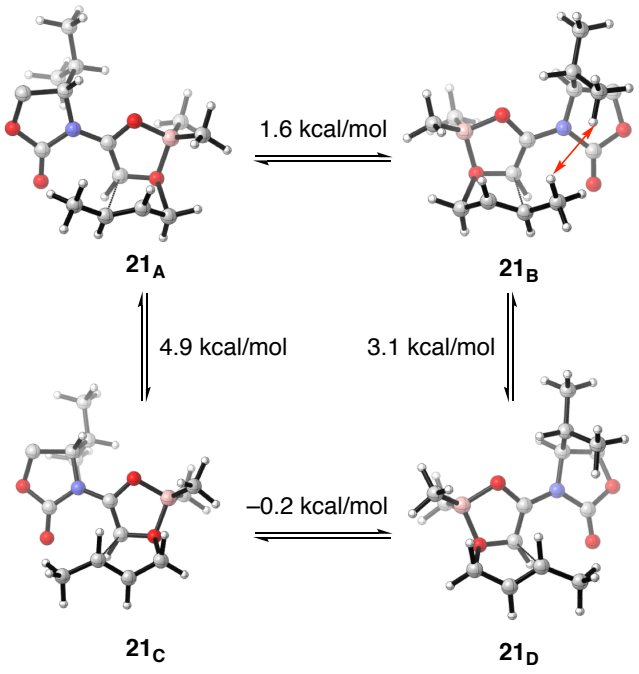
The chelation serves several purposes. In theory it provides organization for stereocontrol, which bore no fruit for substrate **1a** owing to an absence of stereochemically determining interactions. It also, however, allows for a smooth transition from enolate **15** to alkoxide **16** with minimal atomic movement or charge development. Contrast this with the developing charge in transition structure **19** derived from chelate **14.** The ether-based chelate also may competitively inhibit the boron-assisted deacylation via a transition structure such as **20**.



Optimizing Stereoselectivity. The near stereorandom rearrangement of **1a** and computational support for this observed stereorandomness amounted to an inauspicious first effort. It would be more expedient to carry out a simple allylation of a-alkoxy Evans enolates via direct allylation.[16] However, inspection of the cyclic transition structures (Scheme 3.1), along with follow-up computational studies, led us to hypothesize that improved stereocontrol might be achieved through installation of a vinylic substituent at the 3-position (R^2) and replacement of the oxazolidinone benzyl group with an isopropyl moiety.

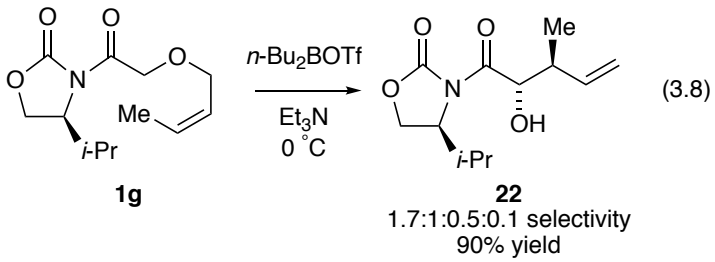
Table 3.1 (entries 2–4) confirmed this supposition. Thus, *trans*-crotyl ether **1c** rearranges to yield a modest 5:1 mixture of **2c** and **3c** to the exclusion of two other possible isomers (entry 3). Rearrangement of the valine-derived variant **1d** occurs with significantly improved 15:1 selectivity (entry 4). The origin of this enhanced selectivity is reflected in the DFT computations (Scheme 3.2). The most stable isomeric transition structure, $\mathbf{21_A}$, corresponds to the major product (**2d**) while the second most stable isomer, $\mathbf{21_B}$, corresponds to the syn product **3d** (eq 3.1). A 2.6 Å CH_3–CH_3 contact in $\mathbf{21_B}$ (see arrow) absent in $\mathbf{21_A}$ appears to be the source of the facial selectivity.

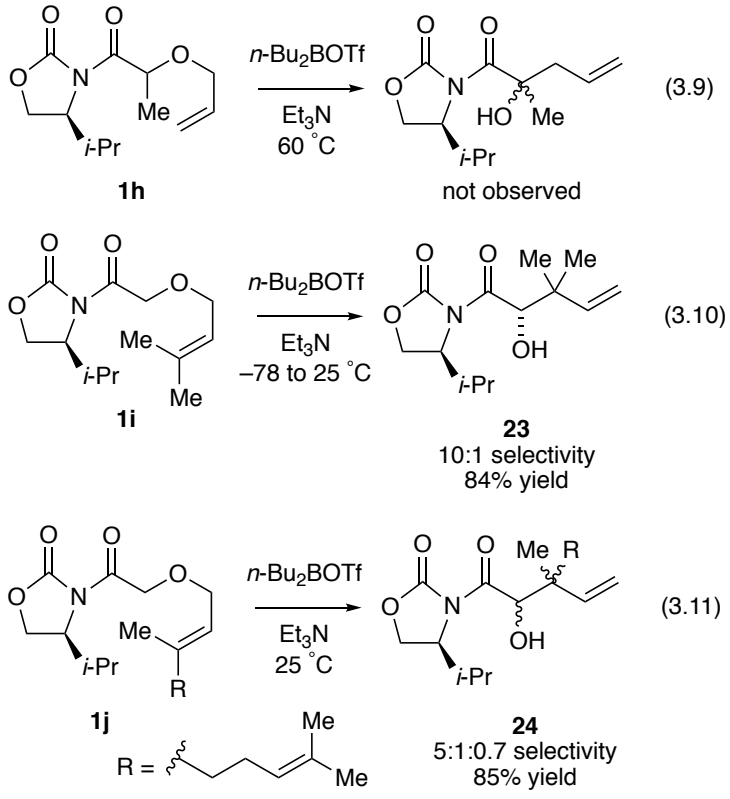
Scheme 3.2. DFT computed stereoisomers of transition structure **21** using methyls as surrogates for *n*-butyls for the rearrangement of **1d** to the major and minor products **2d** and **3d** (Table 3.1, entry 4).



Rearrangement of the *i*-propyl and phenyl-substituted allyl ethers gave excellent results (entries 5 and 6). In the latter case, it was essential to maintain the reaction temperature at –78 °C until after the addition of Et_3N to avoid decomposition of the cinnamyl ether-based substrate **1f** by an apparent solvolysis.

We pressed our luck with a few additional substrates not shown in Table 1. The *cis*-crotyl ether **1g** (eq 3.8) rearranged to give two dominant *anti* isomers albeit with a poor 1.7:1.0:0.5:0.1 stereocontrol. DFT computations are consistent with the modest reversal. Quaternization of the α carbon was largely a disaster (eq 3.9). Quaternization of the b carbon afforded **23** in 10:1 selectivity in high yield (eq 3.10),[17] but that did not translate particularly well to a stereochemically controlled quaternization (eq 3.11).

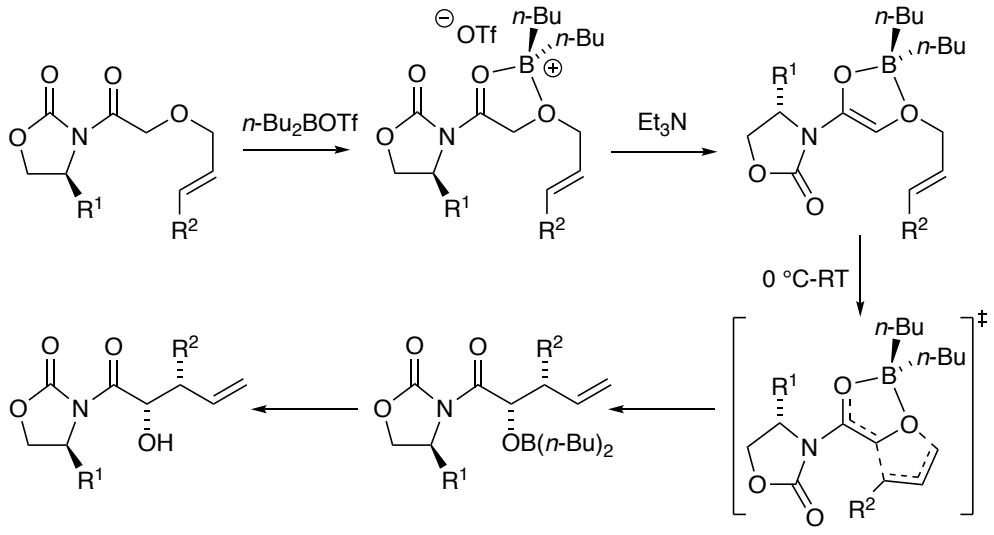




Conclusion

The Evans-boron-enolate-based [2,3]-sigmatropic reaction is an effective protocol using trans allylic ethers and showed some promise for the 2,2-disubstituted allylic ethers. A combination of spectroscopic and computational studies helped us understand the structures of the intermediates along the reaction coordinate (Scheme 3.3) and guided us to a functional protocol where none had seemed to exist in the early stages. The intermediate enolate, chelated by the alkoxy moiety rather than the oxazolidinone carbonyl, is common to a number of boron-based aldol additions of such a-alkoxy Evans enolates.[3,6]

Scheme 3.3. Summary of the boron-enolate based [2,3]-sigmatropic rearrangement.



Experimental

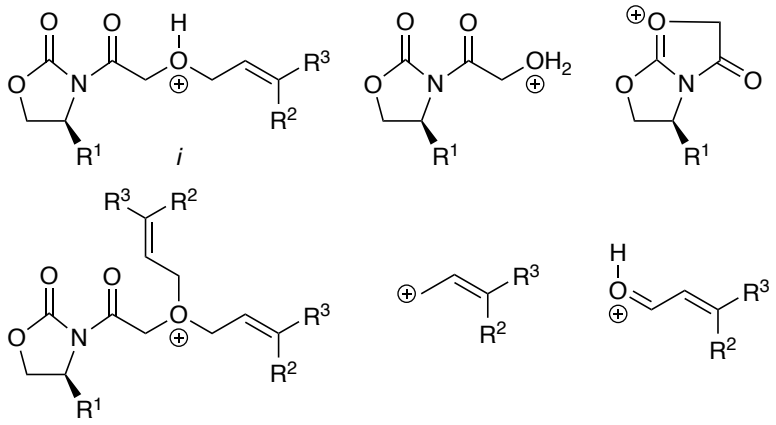
Reagents and Solvents. CH_2Cl_2, $CHCl_3$, and $CDCl_3$ were distilled from molecular sieves. Trialkylamines were distilled from sodium benzophenone ketyl. *n*-Bu_2BOTf was used from a commercial 1.0 M *n*-Bu_2BOTf solution in CH_2Cl_2. Air- and moisture-sensitive materials were manipulated under argon using standard glovebox, vacuum line, and syringe techniques. While the reported yields of rearranged products were optimized, those of the starting materials and correlation products were not.

NMR Spectroscopy. An NMR tube under vacuum was flame-dried on a Schlenk line and allowed to return to room temperature, backfilled with argon, and placed in a –78 °C dry ice/acetone bath. The appropriate amounts of oxazolidinone, *n*-Bu_2BOTf, and Et_3N in $CDCl_3$ were added sequentially via syringe. The tube was flame-sealed under partial vacuum, mixed on a vortex mixer three times for ~10 s with cooling between each vortexing, and stored in a freezer at –80 °C. Standard ^1H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer at 500 and 125 MHz, respectively. The ^1H and ^{13}C resonances are referenced to $CDCl_3$ ($CHCl_3$ 7.26 and $CDCl_3$ 77.2 ppm).

IR spectroscopic analyses. IR spectra were recorded with an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired in 16 scans at a gain of 1 and a resolution of 4 cm^{-1}. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was

capped with a septum for injections and a nitrogen line. After evacuation under full vacuum, heating, and flushing with nitrogen, the flask was charged with CH_2Cl_2 and cooled in a 0 °C ice bath. After a background spectrum was recorded, oxazolidinone **1a** (41.3 mg, 0.15 mmol) was added as a 1.0 M solution in CH_2Cl_2 with stirring, followed by 1.0 M *n*-Bu_2OTf (0.30 mL, 0.30 mmol), and neat Et_3N (70 μL, 0.50 mmol). IR spectra were recorded every 15 s with monitoring of the absorbance at 1783 cm^{-1} and 1825 cm^{-1} over the course of the reaction.

Mass Spectrometry. The high-resolution mass spectra (HRMS) were measured using a DART-Orbitrap. The α-alkoxy oxazolidinones showed relatively minor parent ions (corresponding to ***i*** below) and numerous fragmentation products. The structures listed below are emblematic.



(*S*,*E*)-3-(2-(but-2-en-1-yloxy)acetyl)-4-isopropyloxazolidin-2-one (1d). To a solution of NaHMDS (40 mmol, 7.3 g) in THF (20 mL) was added crotyl alcohol (20 mmol, 1.7 mL, 15:1 *trans*:*cis*) followed by stirring under argon for 15 min at rt. A solution of α-bromo acetic acid (18 mmol, 2.5 g) in THF (10 mL) was added. After stirring for 12 h, the reaction was quenched by KOH solution (1.0 M, 20 mL) and extracted three times with KOH solution. The combined aqueous layers were acidified to pH = 1 using concentrated HCl at 0 ºC and extracted six times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (30% ethyl acetate/hexanes) afforded the acid **4c** as a light yellow oil (1.3 g, 56% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (dqt, *J* = 15.4, 6.6, 1.2 Hz, 1H), 5.58 (dtq, *J* = 15.0, 6.6, 1.6 Hz, 1H), 4.10 (d, *J* = 1.4 Hz, 2H), 4.04 (dp, *J* = 6.6, 1.2 Hz, 2H), 1.73 (ddt, *J* = 6.5, 1.9, 1.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 177.2, 131.8, 126.0, 72.3, 66.6,

17.8. To a solution of **4c** (4.0 mmol, 464.5 mg) in THF (5.0 mL) was added triethylamine (4.4 mmol, 613 µL) followed by stirring for 5 min at –78 ºC. Trimethylacetyl chloride (4.4 mmol, 542 µL) was added. The mixture was warmed to rt and stirred for additional 30 min to generate the mixed anhydride. To a solution of (*S*)-4-isopropyl-2-oxazolidinone (4.0 mmol, 516.6 mg) in THF (30 mL) was added *n*-BuLi (4.0 mmol, 2.5 mL) as a 1.6 M solution in hexane followed by stirring under argon for 15 min at –78 ºC. The mixed anhydride solution was cooled to –78 ºC, and the solution containing the lithiated oxazolidinone was added by cannula. The reaction was warmed to rt and stirred for additional 30 min. The mixture was quenched with saturated NH_4Cl solution and extracted three times with diethyl ether. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (25% ethyl acetate/hexanes) afforded **1d** as a colorless oil (673 mg, 70% yield, 15:1 *trans*:*cis*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 – 5.72 (m, 1H), 5.62 (dtd, *J* = 15.2, 6.5, 1.7 Hz, 1H), 4.64 (d, *J* = 2.3 Hz, 2H), 4.45 (dt, *J* = 8.5, 3.6 Hz, 1H), 4.34 (t, *J* = 8.7 Hz, 1H), 4.26 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.09 – 4.00 (m, 2H), 2.43 (heptd, *J* = 7.3, 3.1 Hz, 1H), 1.72 (d, *J* = 6.6, 3H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.4, 154.2, 131.1, 126.8, 72.3, 69.3, 64.6, 58.3, 28.4, 18.0, 17.9, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{12}H_{20}NO_4$ 242.1386, found 242.1399.

(*S*)-3-(2-(allyloxy)acetyl)-4-benzyloxazolidin-2-one (1a). Following the procedure of **1d** using allyl alcohol and (*S*)-4-benzyl-2-oxazolidinone afforded alkoxy acid **4a** as a yellow liquid (273.1 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 17.2, 10.3, 5.9 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.27 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.15 – 4.10 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.7, 133.3, 119.01, 72.7, 66.7. Further conversion of **4a** affords **1a** as a colorless oil (520.3 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (tt, *J* = 6.9, 1.1 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 5.97 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.35 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.74 – 4.64 (m, 3H), 4.33 – 4.26 (m, 1H), 4.24 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.34 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.82 (dd, *J* = 13.5, 9.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.4, 153.6, 135.1, 134.0, 129.6, 129.2, 127.6, 118.4, 72.7, 69.7, 67.4, 55.0, 37.9. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1230, found 276.1244.

(*S*)-3-(2-(allyloxy)acetyl)-4-isopropyloxazolidin-2-one (1b). Following the procedure of **1d** using allyl acohol afforded **1b** as a colorless oil (543.8 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 16.4, 10.3, 5.8 Hz, 1H), 5.32 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.27 – 5.20 (m, 1H), 4.68 (d, *J* = 3.5 Hz, 2H), 4.45 (dt, *J* = 8.3, 3.5 Hz, 1H), 4.35 (t, *J* = 8.8 Hz, 1H), 4.27 (dd, *J* = 9.2, 3.1 Hz, 1H), 4.18 – 4.08 (m, 2H), 2.43 (hd, *J* = 7.0, 3.9 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 154.2, 134.0, 77.4, 72.7, 69.7, 64.6, 58.4, 28.4, 18.1, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{11}H_{18}NO_4$ 228.1230, found 228.1242.

(*S*,*E*)-4-benzyl-3-(2-(but-2-en-1-yloxy)acetyl)oxazolidin-2-one (1c). Following the procedure to prepare **1d** using (*S*)-4-benzyl-2-oxazolidinone afforded **1c** as a colorless oil (504.3 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.21 (dd, *J* = 7.0, 1.8 Hz, 2H), 5.84 – 5.75 (m, 1H), 5.64 (dtq, *J* = 14.7, 6.3, 1.6 Hz, 1H), 4.73 – 4.67 (m, 1H), 4.65 (d, *J* = 4.3 Hz, 2H), 4.29 (dd, *J* = 9.2, 7.8 Hz, 1H), 4.23 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.33 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.82 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.74 (dq, *J* = 6.5, 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 153.6, 135.1, 131.1, 129.6, 129.2, 127.6, 126.8, 72.4, 69.4, 67.4, 55.0, 37.9, 18.0. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{16}H_{20}NO_4$ 290.1387, found 290.1397.

(*S*,*E*)-4-isopropyl-3-(2-((4-methylpent-2-en-1-yl)oxy)acetyl)oxazolidin-2-one (1e). *trans*-4-Methylpent-2-en-1-ol was prepared by a literature procedure as follows.[18] To a solution of ethyl (triphenylphosphoranylidene)acetate (20 mmol, 6.97 g) in CH_2Cl_2 (40 mL) was added isobutyraldehyde (25 mmol, 2.3 mL) and stirred at rt overnight. The mixture was concentrated in vacuo, dissolved in hexanes, and filtered. The solution was concentrated in vacuo to afford the ester precursor as a colorless liquid (1.2 g, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 15.7, 6.6 Hz, 1H), 5.76 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.45 (dpd, *J* = 13.5, 6.8, 1.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.2, 155.6, 118.8, 60.3, 31.1, 21.4, 14.4. To a solution of the ester (8.5 mmol, 1.2 g) in toluene (20 mL) was added diisobutylaluminum hydride (20 mmol, 20 mL) as 1.0 M solution in toluene at –78 ºC. The reaction was warmed to rt and stirred for additional 12 h. The reaction was quenched with saturated NH_4Cl and acidified with concentrated HCl until

all solid dissolved. The mixture was extracted three times with diethyl ether. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo to afford the alcohol precursor as a colorless liquid (648 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (ddt, *J* = 15.4, 6.2, 1.2 Hz, 1H), 5.59 (dtd, *J* = 15.5, 5.8, 1.2 Hz, 1H), 4.09 (dt, *J* = 6.0, 1.1 Hz, 2H), 2.36 (s, 1H), 2.34 – 2.26 (m, 1H), 1.00 (dd, *J* = 6.7, 0.8 Hz, 6H). Following the procedure of **1d**, *trans*-4-Methylpent-2-en-1-ol was converted to alkoxy acid **4e** as a light yellow liquid (312 mg, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (ddt, *J* = 15.5, 6.5, 1.2 Hz, 1H), 5.50 (dtd, *J* = 15.5, 6.5, 1.4 Hz, 1H), 4.09 (s, 2H), 4.06 (dt, *J* = 6.6, 1.0 Hz, 2H), 2.38 – 2.27 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.45, 144.01, 121.83, 72.62, 66.33, 30.94, 22.21. Alkoxy acid **4e** was converted to **1e** as a colorless liquid (295 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 15.5, 6.4, 1.2 Hz, 1H), 5.57 (dtd, *J* = 15.6, 6.4, 1.4 Hz, 1H), 4.67 (d, *J* = 1.8 Hz, 2H), 4.50 – 4.45 (m, 1H), 4.37 (t, *J* = 8.8 Hz, 1H), 4.29 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.12 – 4.05 (m, 2H), 2.46 (heptd, *J* = 7.0, 3.9 Hz, 1H), 2.40 – 2.29 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 154.1, 143.0, 122.4, 72.4, 69.3, 64.4, 58.2, 30.8, 28.2, 22.1, 22.1, 17.9, 14.7. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{14}H_{24}NO_4$ 270.1700, found 270.1707.

(*S*)-3-(2-(cinnamyloxy)acetyl)-4-isopropyloxazolidin-2-one (1f). Following the procedure of **1d** using cinnamyl alcohol afforded **4f** as a yellow solid (488 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.27 (m, 1H), 6.67 – 6.62 (m, 1H), 6.28 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.29 (dd, *J* = 6.4, 1.3 Hz, 2H), 4.17 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.4, 136.2, 134.6, 128.8, 128.3, 126.8, 124.2, 72.4, 66.6. And **1f** as a light yellow solid (283 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.32 (td, *J* = 7.6, 1.7 Hz, 2H), 7.24 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.33 (dtd, *J* = 15.9, 6.3, 1.7 Hz, 1H), 4.72 (d, *J* = 2.1 Hz, 2H), 4.45 (dt, *J* = 8.1, 3.3 Hz, 1H), 4.34 – 4.24 (m, 4H), 2.47 – 2.37 (m, 1H), 0.92 (dd, *J* = 7.1, 1.6 Hz, 3H), 0.86 (dd, *J* = 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2, 154.1, 136.4, 133.6, 128.6, 127.9, 126.6, 125.0, 72.2, 69.5, 64.4, 58.2, 28.3, 17.9, 14.6. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{17}H_{22}NO_4$ 304.1543, found 304.1557.

(*S*,*Z*)-3-(2-(but-2-en-1-yloxy)acetyl)-4-isopropyloxazolidin-2-one (1g). Following the procedure of **1d** except using 2-butyn-1-ol afforded the alkoxy acid **4g** as a light yellow liquid (805 mg, 33% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 (q, *J* = 2.4 Hz, 2H), 4.23 (s, 2H), 1.86 (t, *J* = 2.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 174.3, 84.6, 73.6, 65.8, 59.3, 3.7. Alkoxy acid **4g** was converted to the acylated oxazolidinone as a colorless oil (987 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (s, 2H), 4.48 – 4.42 (m, 1H), 4.35 (t, *J* = 8.7 Hz, 1H), 4.30 – 4.24 (m, 3H), 2.42 (heptd, *J* = 7.0, 4.0 Hz, 1H), 1.85 (t, *J* = 2.3 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 169.95, 154.2, 83.9, 74.2, 68.6, 64.6, 59.1, 58.4, 28.4, 18.0, 14.8, 3.8. Lindlar hydrogenation was carried out according to a modified literature procedure as follows.[19] To a solution of acylated oxazolidinone (2 mmol, 479 mg) in MeOH (10 mL) was added Lindlar catalyst (0.10 mmol, 212 mg) and stirred under H_2 (1.0 atm) at rt for 18 hr. The reaction was filtered through Celite and concentrated in vacuo. Flash chromatography (25% ethyl acetate/hexanes, Rf = 0.30) afforded **1g** as colorless oil (409 mg, 85%, 12:1 *cis*:*trans*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dqt, *J* = 10.9, 6.9, 1.3 Hz, 1H), 5.65 – 5.58 (m, 1H), 4.66 (d, *J* = 4.5 Hz, 2H), 4.46 (ddd, *J* = 8.3, 4.0, 3.1 Hz, 1H), 4.34 (dd, *J* = 9.2, 8.5 Hz, 1H), 4.26 (dd, *J* = 9.2, 3.0 Hz, 1H), 4.24 – 4.15 (m, 2H), 2.44 (dtt, *J* = 14.0, 7.0, 3.5 Hz, 1H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.4, 154.2, 129.3, 126.0, 69.6, 66.7, 64.6, 58.3, 28.4, 18.0, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{12}H_{20}NO_4$ 242.1387, found 242.1396.

(4*S*)-3-(2-(allyloxy)propanoyl)-4-isopropyloxazolidin-2-one (1h). To a solution of **1b** (0.50 mmol, 114 mg) in THF (3 mL) was added NaHMDS (0.6 mmol, 110 mg) in THF (2 mL) under argon at –78 ºC. After stirring for 15 min, methyl iodide (1.0 mmol, 62 μL) was added and the mixture was warmed to 0 ºC and stirred for another 30 min. The reaction was quenched with NH_4Cl and extracted three times with diethyl ether. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (25% ethyl acetate/hexanes, Rf = 0.30) afforded **1h** as a colorless oil (65 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (ddt, *J* = 17.2, 10.3, 5.8 Hz, 1H), 5.29 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, *J* = 10.3, 1.3 Hz, 1H), 5.11 (q, *J* = 6.6 Hz, 1H), 4.51 (ddd, *J* = 8.5, 4.1, 3.2 Hz, 1H), 4.34 (t, *J* = 8.8 Hz, 1H), 4.25 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.07

(ddt, J = 12.3, 5.8, 1.4 Hz, 1H), 3.92 (ddt, J = 12.3, 6.0, 1.3 Hz, 1H), 2.34 (pd, J = 6.9, 4.1 Hz, 1H), 1.49 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 173.7, 153.7, 134.4, 117.9, 73.7, 71.3, 64.3, 58.3, 28.6, 19.0, 18.0, 15.0. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{12}H_{20}NO_4$ 242.1387, found 242.1399.

(*S*)-4-isopropyl-3-(2-((3-methylbut-2-en-1-yl)oxy)acetyl)oxazolidin-2-one (1i). Following the procedure of **1d** except using 3-methyl-2-buten-1-ol afforded **4i** as a pale oil (573 mg, 40% yield) .^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (tp, J = 7.1, 1.4 Hz, 1H), 4.11 (d, J = 7.2 Hz, 2H), 4.09 (s, 2H), 1.77 (d, J = 1.5 Hz, 3H), 1.70 (d, J = 1.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.64, 139.50, 119.59, 67.89, 66.44, 25.96, 18.17. And **1i** as a white solid (183.5 mg, 36% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (tdt, J = 5.7, 2.8, 1.5 Hz, 1H), 4.65 (d, J = 2.9 Hz, 2H), 4.46 (dt, J = 8.3, 3.5 Hz, 1H), 4.34 (t, J = 8.8 Hz, 1H), 4.26 (dd, J = 9.1, 3.1 Hz, 1H), 4.12 (qd, J = 11.4, 7.1 Hz, 3H), 2.44 (pd, J = 7.0, 3.9 Hz, 1H), 1.76 (d, J = 1.5 Hz, 3H), 1.70 (d, J = 1.4 Hz, 3H), 0.93 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.5, 154.2, 138.6, 120.3, 69.5, 67.9, 64.5, 58.3, 28.4, 26.0, 18.2, 18.1, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{13}H_{22}NO_4$ 256.1543, found 256.1556.

(*S*,*E*)-3-(2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)acetyl)-4-isopropyloxazolidin-2-one (1j). Following the procedure of **1d** using geraniol afforded **4j** as a colorless oil (835 mg, 39% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (t, J = 7.1 Hz, 1H), 5.08 (t, J = 7.1 Hz, 1H), 4.14 (d, J = 7.1 Hz, 2H), 4.08 (s, 2H), 2.11 (t, J = 7.1 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.68 (d, J = 2.3 Hz, 6H), 1.60 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 173.7, 142.9, 132.1, 123.8, 119.2, 67.9, 66.3, 39.7, 26.4, 25.8, 17.8, 16.6. Conversion of **4j** to **1j** afforded a colorless oil (468 mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (ddt, J = 8.3, 7.0, 1.3 Hz, 1H), 5.15 – 5.08 (m, 1H), 4.68 (d, J = 2.6 Hz, 2H), 4.48 (dt, J = 8.3, 3.5 Hz, 1H), 4.37 (t, J = 8.8 Hz, 1H), 4.29 (dd, J = 9.2, 3.1 Hz, 1H), 4.17 (qd, J = 11.5, 6.9 Hz, 2H), 2.46 (heptd, J = 7.1, 3.9 Hz, 1H), 2.17 – 2.10 (m, 2H), 2.07 (dd, J = 9.4, 6.1 Hz, 2H), 1.71 (d, J = 1.4 Hz, 3H), 1.70 (d, J = 1.4 Hz, 3H), 1.62 (s, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.5, 154.2, 141.8, 131.9, 124.0, 120.0, 69.5, 68.0, 64.5, 58.3, 39.8, 28.4, 26.5, 25.8, 18.1, 17.8,

16.7, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{18}H_{30}NO_4$ 324.2169, found 324.2185.

(*S*)-3-((2*S*,3*R*)-2-hydroxy-3-methylpent-4-enoyl)-4-isopropyloxazolidin-2-one (2d). To a solution of **1d** (0.40 mmol, 96.4 mg) in CH_2Cl_2 (1.0 mL) was added *n*-Bu_2BOTf (0.80 mmol, 800 μL) as 1.0 M solution in CH_2Cl_2 followed by stirring at 0 ºC for 5 min. Triethyamine (1.2 mmol, 168 μL) was added. The reaction was warmed to rt and stirred for an additional 3 h. The reaction was quenched with saturated NH_4Cl and extracted three times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (20% ethyl acetate/hexanes) afforded **2d** and its minor isomer as colorless oil (78.9 mg, 82% yield, 15:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.6, 10.3, 7.6 Hz, 1H), 5.13 – 5.02 (m, 3H), 4.38 (dt, *J* = 7.2, 3.4 Hz, 1H), 4.30 (t, *J* = 8.4 Hz, 1H), 4.26 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.31 (d, *J* = 8.9 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.44 (heptd, *J* = 7.2, 3.7 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.3, 153.9, 140.0, 115.5, 73.8, 64.2, 59.2, 41.8, 28.4, 18.1, 14.6, 13.9. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{12}H_{20}NO_4$ 242.1387, found 242.1399.

(*S*)-4-benzyl-3-((*S*)-2-hydroxypent-4-enoyl)oxazolidin-2-one (2a). Following the procedure for **1d**, **1a** afforded **2a** and its minor isomer as colorless oil (90% yield, 2:1 selectivity). Major product ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.19 (m, 2H), 5.87 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.21 – 5.09 (m, 3H), 4.66 (ddt, *J* = 10.0, 6.7, 3.3 Hz, 1H), 4.31 – 4.23 (m, 2H), 3.55 (d, *J* = 7.9 Hz, 1H), 3.32 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.84 (dd, *J* = 13.5, 9.4 Hz, 1H), 2.62 (dddt, *J* = 14.3, 7.1, 4.7, 1.3 Hz, 1H), 2.46 (dtt, *J* = 14.2, 7.1, 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.1, 153.4, 134.9, 133.0, 129.6, 129.2, 127.7, 118.8, 70.4, 67.1, 55.7, 38.4, 37.7. Minor product ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.19 (m, 2H), 5.87 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.23 – 5.14 (m, 3H), 4.75 (ddt, *J* = 9.8, 8.1, 3.5 Hz, 1H), 4.31 (t, *J* = 8.6 Hz, 1H), 4.24 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.35 – 3.25 (m, 2H), 2.74 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.67 (dddd, *J* = 11.3, 5.8, 2.5, 1.2 Hz, 1H), 2.53 – 2.45 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.7, 153.1, 134.9, 132.6, 129.5, 129.2, 127.7, 119.1, 70.3, 67.3, 55.2, 39.1, 38.3. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1230, found 276.1243.

(*S*)-3-((*S*)-2-hydroxypent-4-enoyl)-4-isopropyloxazolidin-2-one (2b). Following the procedure for **1d**, **1b** afforded **2b** and its minor isomer (81% yield, 3:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.19 – 5.06 (m, 3H), 4.41 (dt, *J* = 7.7, 3.3 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 4.29 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 1H), 2.59 (dddt, *J* = 14.3, 7.1, 4.9, 1.3 Hz, 1H), 2.48 – 2.38 (m, 2H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.0, 154.1, 133.1, 118.6, 70.4, 64.4, 59.1, 38.4, 28.4, 18.1, 14.7. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{11}H_{18}NO_4$ 228.1230, found 228.1243.

(*S*)-4-benzyl-3-((2*S*,3*R*)-2-hydroxy-3-methylpent-4-enoyl)oxazolidin-2-one (2c). Following the procedure for **1d** using **1c** afforded **2c** and its minor isomer as colorless oil (90% yield, 5:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 5.89 (ddd, *J* = 17.5, 10.3, 7.5 Hz, 1H), 5.16 – 5.06 (m, 3H), 4.64 (ddt, *J* = 9.6, 6.4, 3.5 Hz, 1H), 4.26 – 4.23 (m, 2H), 3.37 – 3.30 (m, 2H), 2.82 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.66 – 2.58 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.4, 153.2, 139.9, 135.0, 129.6, 129.2, 127.7, 115.6, 73.9, 67.0, 55.8, 41.8, 37.7, 13.9. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{16}H_{20}NO_4$ 290.1386, found 290.1398.

(*S*)-3-((2*S*,3*R*)-2-hydroxy-3-isopropylpent-4-enoyl)-4-isopropyloxazolidin-2-one (2e). Following the procedure for rearrangement of **1d**, **1e** afforded **2e** (71% yield, >30:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (dt, *J* = 17.1, 10.1 Hz, 1H), 5.23 (t, *J* = 9.8 Hz, 1H), 5.08 (dd, *J* = 10.3, 2.2 Hz, 1H), 5.02 (dd, *J* = 17.1, 2.2 Hz, 1H), 4.33 (q, *J* = 4.7 Hz, 1H), 4.24 (d, *J* = 4.8 Hz, 2H), 3.18 (d, *J* = 10.2 Hz, 1H), 2.39 (heptd, *J* = 7.0, 3.7 Hz, 1H), 2.24 (dddd, *J* = 19.2, 13.1, 8.3, 3.5 Hz, 2H), 0.92 (dd, *J* = 6.9, 1.4 Hz, 6H), 0.89 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.0, 154.4, 134.5, 118.8, 71.9, 64.3, 59.1, 56.5, 28.7, 26.9, 21.5, 18.2, 16.7, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{14}H_{24}NO_4$ 270.1670, found 270.1712.

(*S*)-3-((2*S*,3*S*)-2-hydroxy-3-phenylpent-4-enoyl)-4-isopropyloxazolidin-2-one (2f). To a solution of **1f** (0.040 mmol, 12.1 mg) in CH_2Cl_2 (1.0 mL) was added *n*-Bu_2BOTf (0.080 mmol, 80 μL) as 1.0 M solution in CH_2Cl_2 followed by stirring at –78 ºC for 5 min. Triethylamine (0.12 mmol, 17 μL) was added. The reaction was warmed to rt and stirred for additional 3 h. The reaction was quenched with saturated NH_4Cl and

extracted three times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (20% ethyl acetate/hexanes) afforded **2f** and its minor isomer (11.2 mg, 91% yield, >30:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 6.19 (ddd, *J* = 17.1, 10.2, 8.2 Hz, 1H), 5.58 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.20 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.17 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.33 – 4.23 (m, 3H), 3.78 – 3.71 (m, 1H), 3.21 (d, *J* = 9.2 Hz, 1H), 2.40 (heptd, *J* = 7.0, 3.5 Hz, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.7, 154.0, 138.9, 137.4, 128.7, 128.6, 127.5, 117.3, 73.7, 64.3, 59.3, 54.5, 28.4, 18.1, 14.7. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{17}H_{22}NO_4$ 304.1543, found 304.1558.

(4*S*)-3-(2-hydroxy-3-methylpent-4-enoyl)-4-isopropyloxazolidin-2-one (22). Following the procedure for rearrangement of **1d**, **1g** afforded **22** and its minor isomers (90% yield, 1.7:1:0.5:0.1 selectivity). Major product ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 17.1, 10.4, 8.0 Hz, 1H), 5.11 – 5.05 (m, 3H), 4.38 – 4.35 (m, 1H), 4.33 – 4.30 (m, 1H), 4.30 – 4.28 (m, 1H), 3.19 (d, *J* = 8.6 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.48 (dtd, *J* = 14.1, 7.0, 3.6 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.93 (dd, *J* = 7.1, 1.6 Hz, 3H), 0.89 (dd, *J* = 6.9, 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.3, 153.8, 137.6, 116.6, 74.4, 64.3, 59.4, 41.4, 28.3, 18.1, 17.0, 14.6. Minor product ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 – 5.70 (m, 1H), 5.10 – 5.06 (m, 2H), 5.04 (ddd, *J* = 17.2, 1.9, 1.2 Hz, 1H), 4.52 (dt, *J* = 8.6, 3.4 Hz, 1H), 4.37 – 4.34 (m, 1H), 4.29 – 4.26 (m, 1H), 3.01 (d, *J* = 8.9 Hz, 1H), 2.78 (dtdd, *J* = 9.4, 8.3, 6.5, 2.6 Hz, 1H), 2.26 (heptd, *J* = 6.8, 3.4 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 0.94 – 0.92 (m, 3H), 0.90 – 0.89 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.8, 153.5, 136.9, 117.1, 74.1, 64.2, 58.3, 42.0, 28.7, 18.1, 17.7, 14.9. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{12}H_{20}NO_4$ 242.1387, found 242.1399.

(*S*)-3-((*S*)-2-hydroxy-3,3-dimethylpent-4-enoyl)-4-isopropyloxazolidin-2-one (23). To a solution of **1i** (0.10 mmol, 25.5 mg) in CH_2Cl_2 (1.0 mL) was added *n*-Bu_2BOTf (0.15 mmol, 150 μL) as 1.0 M solution in CH_2Cl_2 followed by stirring at –78 ºC for 5 min. Triethylamine (0.30 mmol, 42 μL) was added. The reaction was warmed to rt and stirred for additional 12 h. The reaction was quenched with saturated NH_4Cl and extracted three times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (20% ethyl acetate/hexanes) afforded **23**

and its minor isomer (21.3 mg, 84% yield, 10:1 selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.06 (dd, *J* = 10.8, 1.3 Hz, 1H), 5.02 (dd, *J* = 17.5, 1.3 Hz, 1H), 4.33 (ddd, *J* = 7.1, 3.9, 2.9 Hz, 1H), 4.26 – 4.20 (m, 2H), 3.10 (d, *J* = 10.0 Hz, 1H), 2.43 (heptd, *J* = 7.0, 3.8 Hz, 1H), 1.15 (s, 3H), 1.08 (s, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.7, 154.1, 143.7, 113.6, 74.7, 64.0, 59.4, 42.3, 28.7, 24.9, 20.7, 18.2, 14.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{13}H_{22}NO_4$ 256.1543, found 256.1556.

(*S*)-3-((2*S*,3*R*)-2-hydroxy-3,7-dimethyl-3-vinyloct-6-enoyl)-4-isopropyloxazolidin-2-one (24). Following the procedure of **1i** using **1j** afforded **24** (85% yield, 5:1:0.7 selectivity). Major ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.73 (m, 1H), 5.27 (dd, *J* = 10.8, 0.8 Hz, 1H), 5.19 (ddd, *J* = 17.5, 4.1, 0.9 Hz, 1H), 5.08 (tdt, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.58 (s, 1H), 4.04 (dt, *J* = 14.8, 7.5 Hz, 1H), 3.84 (dd, *J* = 11.8, 3.1 Hz, 1H), 3.75 (ddd, *J* = 10.1, 8.1, 3.1 Hz, 1H), 2.37 (dp, *J* = 10.2, 6.7 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.74 (ddd, *J* = 13.6, 11.9, 4.8 Hz, 1H), 1.67 (t, *J* = 1.3 Hz, 3H), 1.59 (d, *J* = 1.3 Hz, 3H), 1.58 – 1.54 (m, 1H), 1.21 (s, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.90 – 0.87 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.0, 154.1, 142.4, 131.7, 124.5, 114.9, 74.2, 64.0, 59.5, 46.0, 38.6, 28.8, 25.8, 22.7, 18.2, 17.8, 15.9, 14.9. Minor ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.13 (dd, *J* = 10.9, 1.4 Hz, 1H), 5.10 – 5.05 (m, 1H), 5.00 (dd, *J* = 17.6, 1.5 Hz, 1H), 4.29 (ddd, *J* = 7.8, 3.9, 2.4 Hz, 1H), 4.22 (dd, *J* = 9.1, 2.4 Hz, 1H), 4.19 (dd, *J* = 9.1, 7.8 Hz, 1H), 3.01 (d, *J* = 10.3 Hz, 1H), 2.42 (pd, *J* = 6.9, 3.8 Hz, 1H), 1.90 (dq, *J* = 11.8, 6.2 Hz, 2H), 1.70 – 1.65 (m, 5H), 1.57 (d, *J* = 1.3 Hz, 3H), 1.03 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.7, 155.9, 138.9, 132.3, 123.8, 117.5, 84.2, 61.7, 61.4, 43.8, 36.0, 26.6, 25.8, 22.3, 20.1, 19.9, 18.8, 17.8. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_{18}H_{30}NO_4$ 324.2169, found 324.2182.

(3*S*,4*R*)-3-hydroxy-4-methyldihydrofuran-2(3*H*)-one (6). To a solution of **2d** (0.21 mmol, 50.8 mg) in CH_2Cl_2 cooled to –78 °C, O_3 was bubbled through until the solution turned blue. Dimethyl sulfide (13.5 mmol, 1.0 mL) was added gradually until the blue color disappeared. The mixture was warmed to rt and stirred for another 30 min to ensure complete quenching. The reaction was washed three times with brine, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography (40% ethyl acetate/hexanes)

afforded the corresponding aldehyde (21.3 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 5.32 (dd, *J* = 7.0, 5.3 Hz, 1H), 4.44 (dt, *J* = 3.8, 2.3 Hz, 1H), 4.39 (t, *J* = 8.7 Hz, 1H), 4.32 (dd, *J* = 9.2, 2.6 Hz, 1H), 3.96 (d, *J* = 7.0 Hz, 1H), 2.95 (qd, *J* = 7.3, 5.4 Hz, 1H), 2.42 (dtq, *J* = 11.0, 7.2, 4.0, 3.4 Hz, 1H), 1.15 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.8, 172.2, 154.5, 70.3, 64.7, 59.1, 48.1, 28.4, 18.0, 14.7, 8.5. $NaBH_4$ (1.0 mmol, 37.8 mg) was added to acetic acid (0.5 mL) at 0 ºC, warmed to rt, then stirred for 1.0 hr. The aldehyde in acetic acid (0.20 mL) was added and the mixture stirred for an additional 30 min. The reaction was quenched by saturated $NaHCO_3$ solution and extracted three times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (40% ethyl acetate/hexanes) afforded the cyclized lactone **6** (2 mg, 20%), which was compared to literature data.[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (dd, *J* = 9.1, 7.9 Hz, 1H), 4.01 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.80 (dd, *J* = 10.7, 9.1 Hz, 1H), 2.59 – 2.48 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 177.4, 73.9, 70.7, 39.1, 14.5. $[a]_D^{20}$ –40° (c 1.0, $CDCl_3$). HRMS (DART-Orbitrap) *m/z* $[M+H–H_2O]^+$. calcd for $C_5H_7O_2$ 99.0440, found 99.0446.

(3*S*,4*R*)-3-hydroxy-4-isopropyldihydrofuran-2(3*H*)-one (7). Following the procedure converting **2d** to lactone **6**, **2e** afforded the intermediate aldehyde as a colorless liquid (15 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (d, *J* = 1.5 Hz, 1H), 5.10 – 5.06 (m, 1H), 4.38 (t, *J* = 8.1 Hz, 1H), 4.30 (d, *J* = 6.4 Hz, 2H), 3.09 (ddd, *J* = 9.8, 4.0, 1.5 Hz, 1H), 2.44 (tt, *J* = 7.3, 3.7 Hz, 1H), 2.32 (dqd, *J* = 12.0, 6.6, 3.1 Hz, 1H), 1.21 (d, *J* = 7.3 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.94 (dd, *J* = 7.2, 1.8 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 203.9, 171.6, 155.3, 68.7, 64.9, 59.0, 57.4, 28.7, 26.2, 21.2, 18.6, 18.0, 14.9. And the cyclized lactone **7** as a colorless liquid (2 mg, 28% yield), which was compared to literature data.[12a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (t, *J* = 8.7 Hz, 1H), 4.15 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.89 (dd, *J* = 10.7, 9.2 Hz, 1H), 2.50 (d, *J* = 2.5 Hz, 1H), 2.23 (tt, *J* = 10.5, 8.5 Hz, 1H), 1.78 (ddt, *J* = 14.8, 13.0, 6.6 Hz, 1H), 1.11 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 178.0, 71.8, 68.9, 50.2, 30.9, 20.7, 20.3. HRMS (DART-Orbitrap) *m/z* $[M+H–H_2O]^+$ calcd for $C_7H_{11}O_2$ 127.0754, found 127.0761.

(*S*)-3-hydroxy-4,4-dimethyldihydrofuran-2(3*H*)-one (8). Following the procedure of **6** using **23** afforded the intermediate aldehyde as a white crystal (6.1 mg, 23% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 4.94 (d, *J* = 6.9 Hz, 1H), 4.44 (ddd, *J* = 8.3, 4.1, 2.9 Hz, 1H), 4.37 (dd, *J* = 9.1, 8.3 Hz, 1H), 4.31 – 4.28 (m, 2H), 2.33 (hd, *J* = 6.9, 4.0 Hz, 1H), 1.25 (s, 3H), 1.22 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H). And the cyclized lactone **8** as a colorless oil (3 mg, 96% yield) shown to be identical to a known sample.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.10 (d, *J* = 3.3 Hz, 1H), 4.03 (d, *J* = 9.0 Hz, 1H), 3.94 (d, *J* = 8.9 Hz, 1H), 2.37 (d, *J* = 3.1 Hz, 1H), 1.24 (s, 3H), 1.08 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 176.8, 76.5, 75.9, 41.1, 23.1, 18.9. HRMS (DART-Orbitrap) *m/z* $[M+H]^+$ calcd for $C_6H_{12}O_3$ 131.0703, found 131.0704. $[a._D^{20}$ -33.3° (c 1.2, $CDCl_3$).

(*S*)-butane-1,2,4-triol (5). To a solution of **2a** (0.07 mmol, 18.5 mg) in CH_2Cl_2 cooled to –78 °C, O_3 was bubbled through until the solution turned blue. Dimethyl sulfide (13.5 mmol, 1.0 mL) was added gradually until the blue color disappeared and the mixture was warmed to rt and stirred for another 30 min to ensure the complete quenching. The reaction was extracted three times with brine, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography (50% ethyl acetate/hexanes) afforded the aldehyde as a colorless liquid (5.8 mg, 31% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, *J* = 0.9 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.0, 1.7 Hz, 2H), 4.81 (d, *J* = 4.6 Hz, 1H), 4.69 (ddt, *J* = 10.4, 9.2, 3.0 Hz, 1H), 4.31 (dd, *J* = 9.2, 8.0 Hz, 1H), 4.27 – 4.24 (m, 2H), 3.85 – 3.65 (m, 1H), 3.33 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.85 – 2.81 (m, 1H). To a solution of the aldehyde in MeOH (0.10 mL) was added $NaBH_4$ (0.05 mmol, 2 mg) at 0 ºC and stirred for 1 hr after warming to rt. The reaction was concentrated in vacuo. Flash chromatography (ethyl acetate) afforded the triol **5** as a colorless liquid (1.9 mg, 85%), which was compared with literature data.[11] ^{1}H NMR (500 MHz, D_2O) δ 3.75 (ddt, *J* = 8.5, 6.8, 4.0 Hz, 1H), 3.64 (ddd, *J* = 7.6, 5.9, 1.6 Hz, 2H), 3.52 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.41 (dd, *J* = 11.7, 6.8 Hz, 1H), 1.66 (dtd, *J* = 14.6, 7.3, 4.3 Hz, 1H), 1.56 (ddt, *J* = 14.5, 8.9, 6.0 Hz, 1H). {^{1}H}^{13}C NMR (126 MHz, D_2O) δ 69.0, 65.6, 58.4, 34.7. $[a._D^{20}$ –31.5° (c 1.0, D_2O). HRMS (DART-Orbitrap) *m/z* $[M+H–HOD]^+$ calcd for $C_4H_7D_2O_2$ 91.0723, found 91.0728.

Chapter 3 Appendix

Chapter 3 Appendix Table of Contents

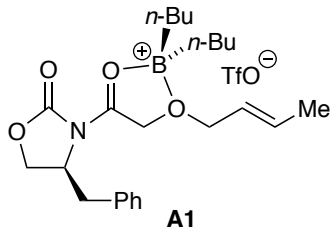
1. IR spectroscopy

2. NMR spectroscopic structural study

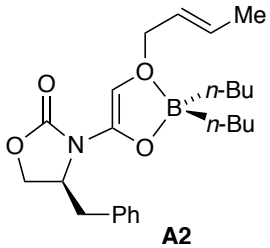
3. Kinetics

4. Syntheses of substrates

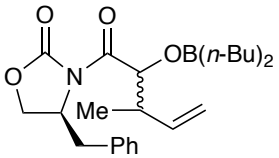
5. Wittig Rearrangements



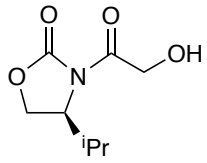
A1



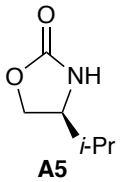
A2



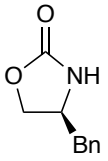
A3



A4



A5



A6

1. IR spectra

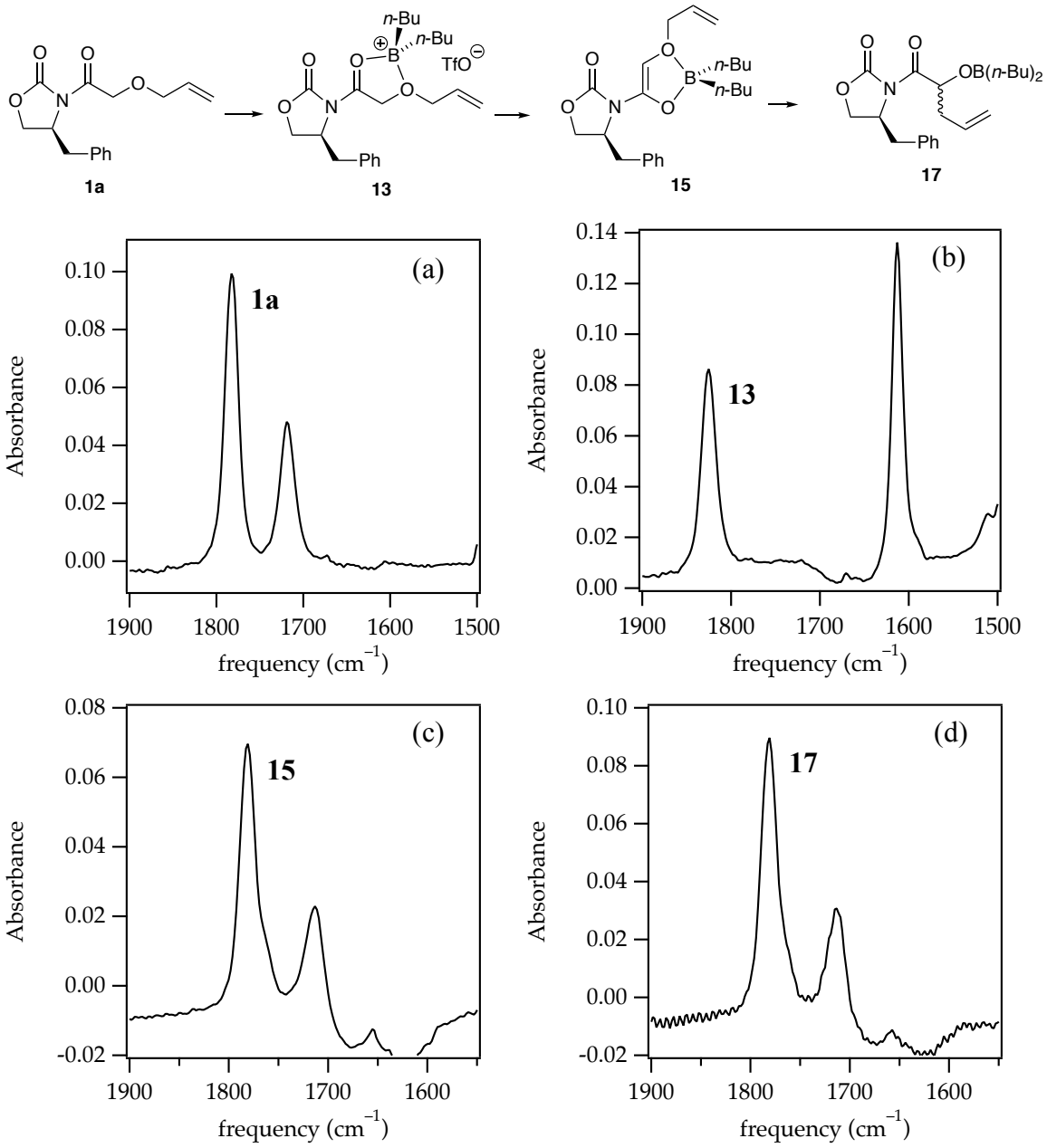


Figure A.3.1. IR spectra of 0.030 M **1a** in CH_2Cl_2 recorded at 0 °C with (a) no additive; (b) 0.060 M *n*-Bu_2BOTf affording **13**; (c) 0.060 M *n*-Bu_2BOTf and 0.10 M Et_3N affording **15**; and (d) product **17** after warming to 25 °C.

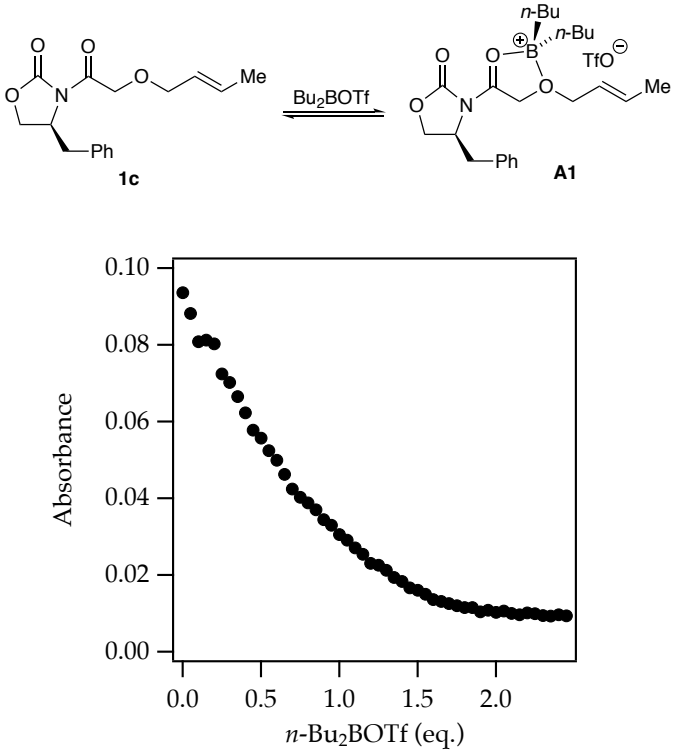


Figure A.3.2. Loss of oxazolidinone carbonyl (1783 cm^{-1}) at –30 ºC of **1c** (0.040 M) in CH_2Cl_2. *n*-Bu_2BOTf (1.0 M) in CH_2Cl_2 via syringe pump over 13 min. The requirement of ≈2.0 equiv of *n*-Bu_2BOTf for full complexation, and the curvature of the decay suggests that the complexation is a soft equilibrium.

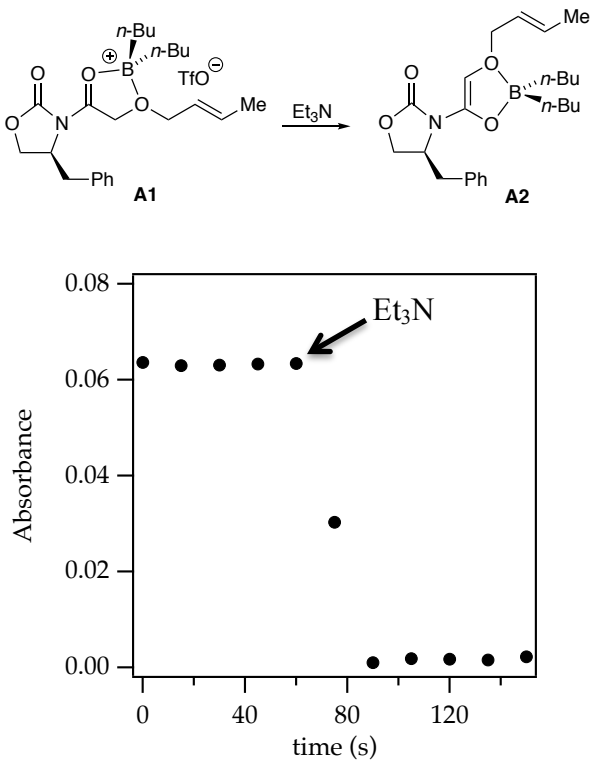


Figure A.3.3. IR spectrum recorded at –30 ºC following the loss of the oxazolidinone carbonyl (1825 cm^{-1}) of boron complex **A1** formed from 0.040 M **1c** and 0.10 M *n*-Bu_2BOTf. Addition of Et_3N (0.12 M) causes immediate disappearance of boron complex **A1** and formation of boron enolate **A2**.

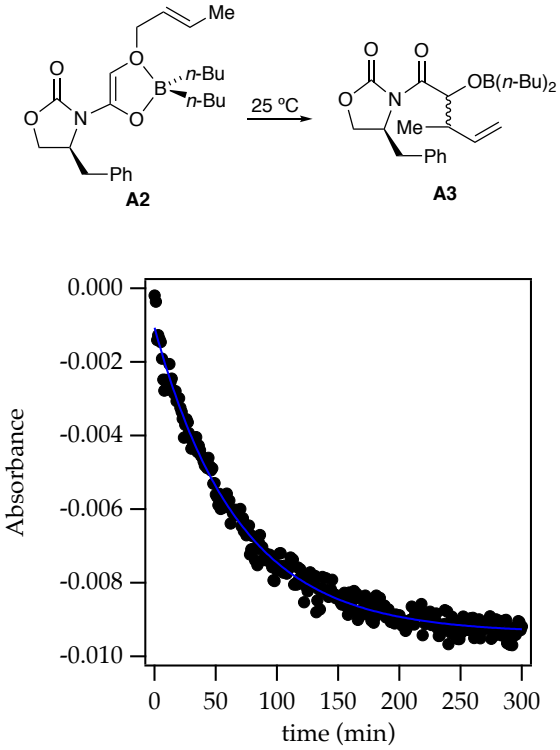
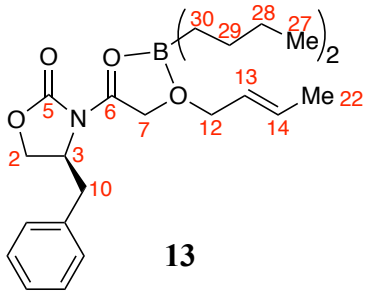


Figure A.3.4. Loss of the oxazolidinone carbonyl of **A2** (1781 cm^{-1}) in a solution of 0.040 M **1c**, 0.10 M *n*-Bu_2BOTf, and 0.12 M Et_3N in CH_2Cl_2. The decay correlates with the enolate rearranging to the product alkoxide **A3**. The lower net absorbance loss compared to enolate is due to peak overlap between enolate and alkoxide. The curve depicts a least-squares fit to $y = a^{-bx} + c$, such that $a = 0.00829 \pm 0.00006$, $b = 0.0147 \pm 0.0002$, $c = 0.00936 \pm 0.00003$.

2. NMR structural study



13

Table A.3.1. ^{1}H and ^{13}C chemical shift assignments for **13**.[a,b]

Atom #	δ ^{13}C, ppm	δ ^{1}H, ppm	COSY	HMBC	ROESY
2	69.8	4.42 (2')	2", 3	10, 3, 5	2", 10"
		4.64 (2")	2', 3		3, 2'
3	56.4	4.88	2', 2", 10', 10"	10, 5	2', 10'
10	36.4	3.35 (10')	10", 3	3, 2	10", 3
		3.00 (10")	10', 3		10', 2'
7	70.7	5.51		12, 6	12, 13
12	78.2	4.70	13, 22	7, 13, 14	30, 7, 13, 14
13	119.5	5.59	14, 12, 22	22, 6	7, 12, 22
14	142.2	6.21	13, 22	22, 12	12, 22
22	18.3	1.81	12, 13, 14	13, 14	13, 14
30	18.5	0.66	29	29	12
29, 28	25.7	1.25	30, 27	27, 30	
27	14.2	0.85	28	28	
5	150.8				
6	175.3				

[a] Important correlations that allowed determination of subunit arrangement are marked in red. [b] *n*-butyl groups time average.

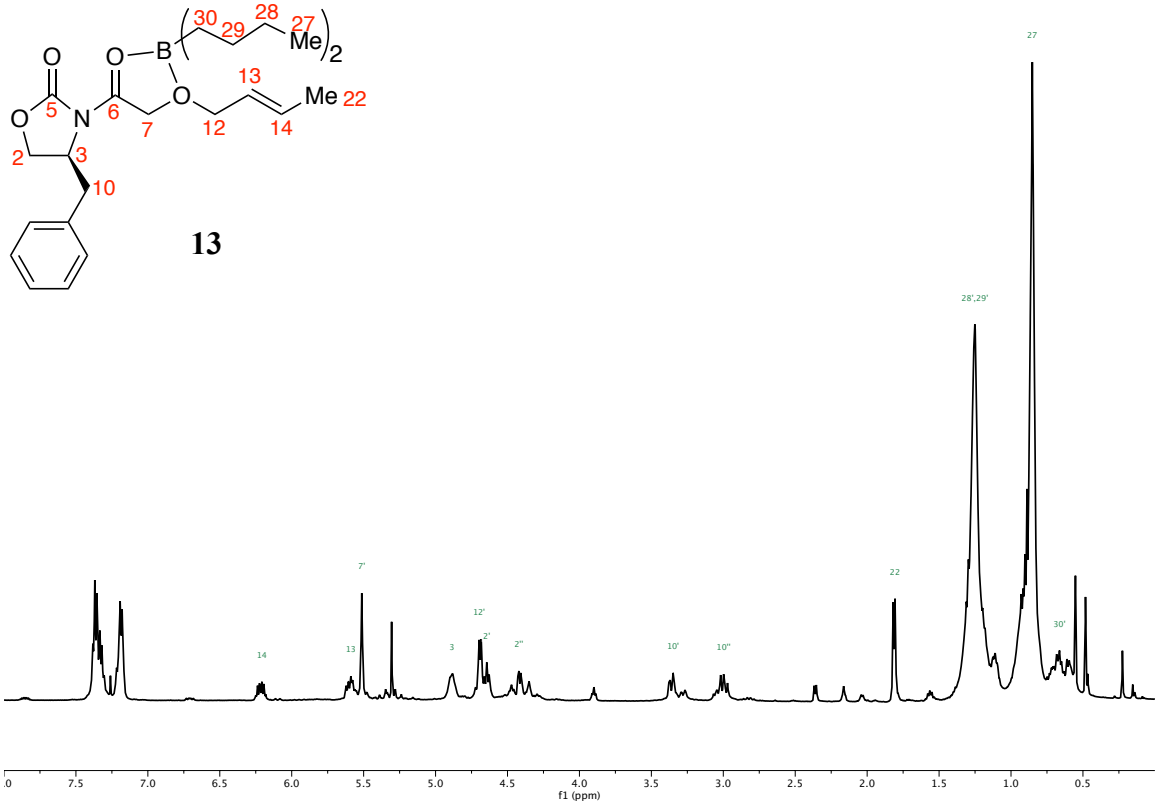


Figure A.3.5. ^{1}H NMR spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

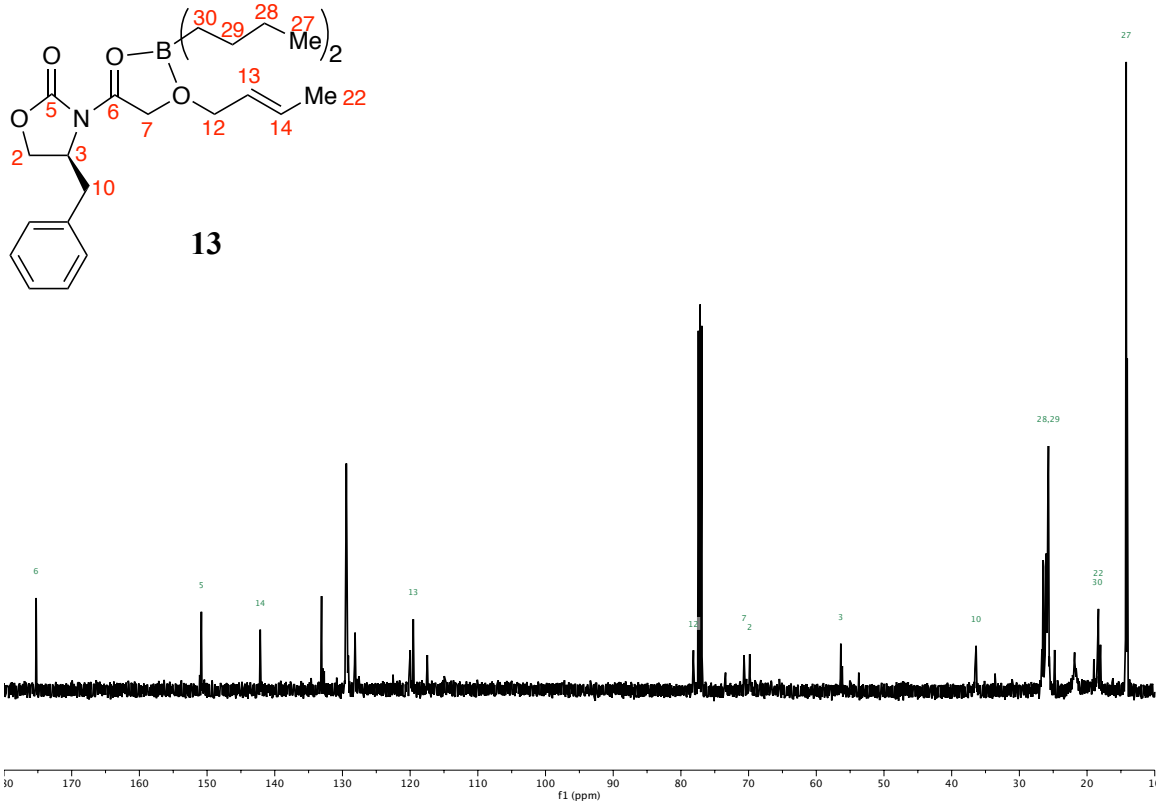
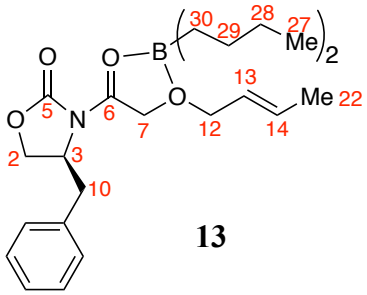


Figure A.3.6. $^{13}C\{^{1}H\}$ NMR spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	HSQCAD
4	Number of Scans	2
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.1501



13

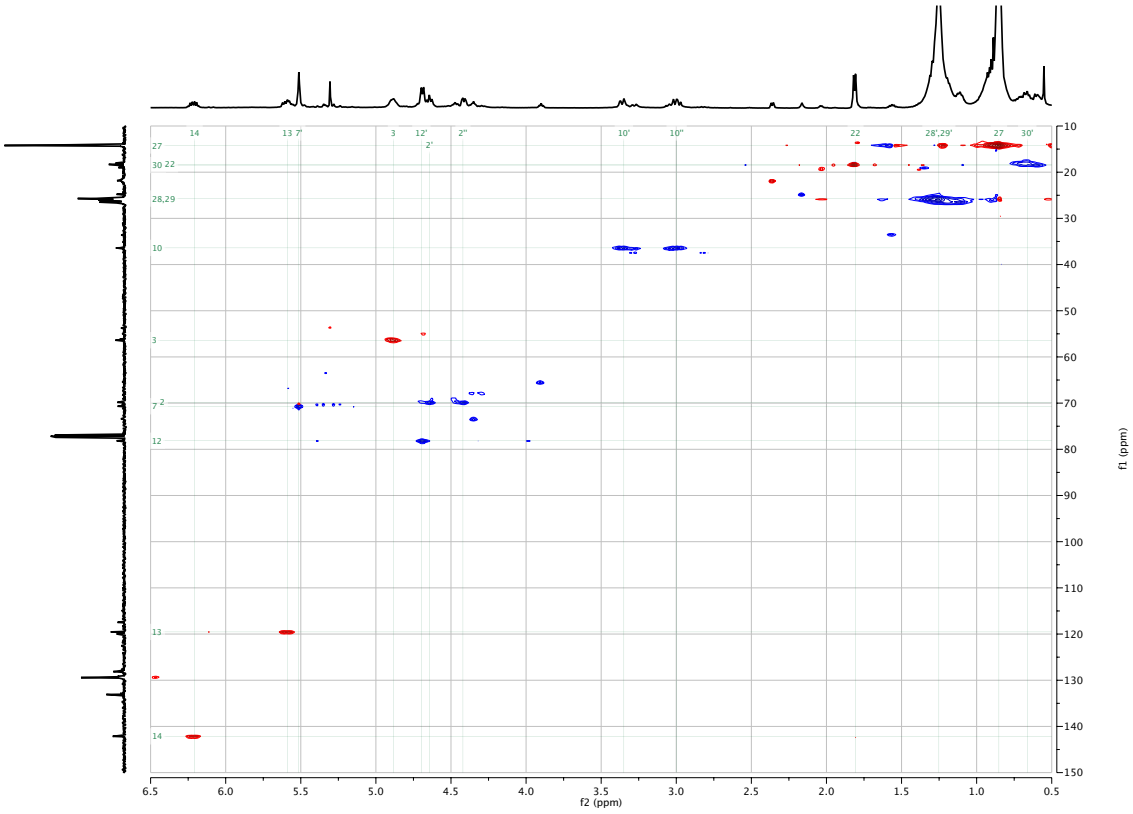
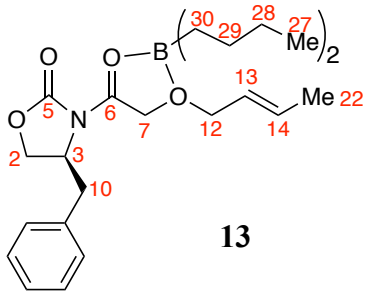


Figure A.3.7. HSQC spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	gCOSY
4	Number of Scans	1
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.5000



13

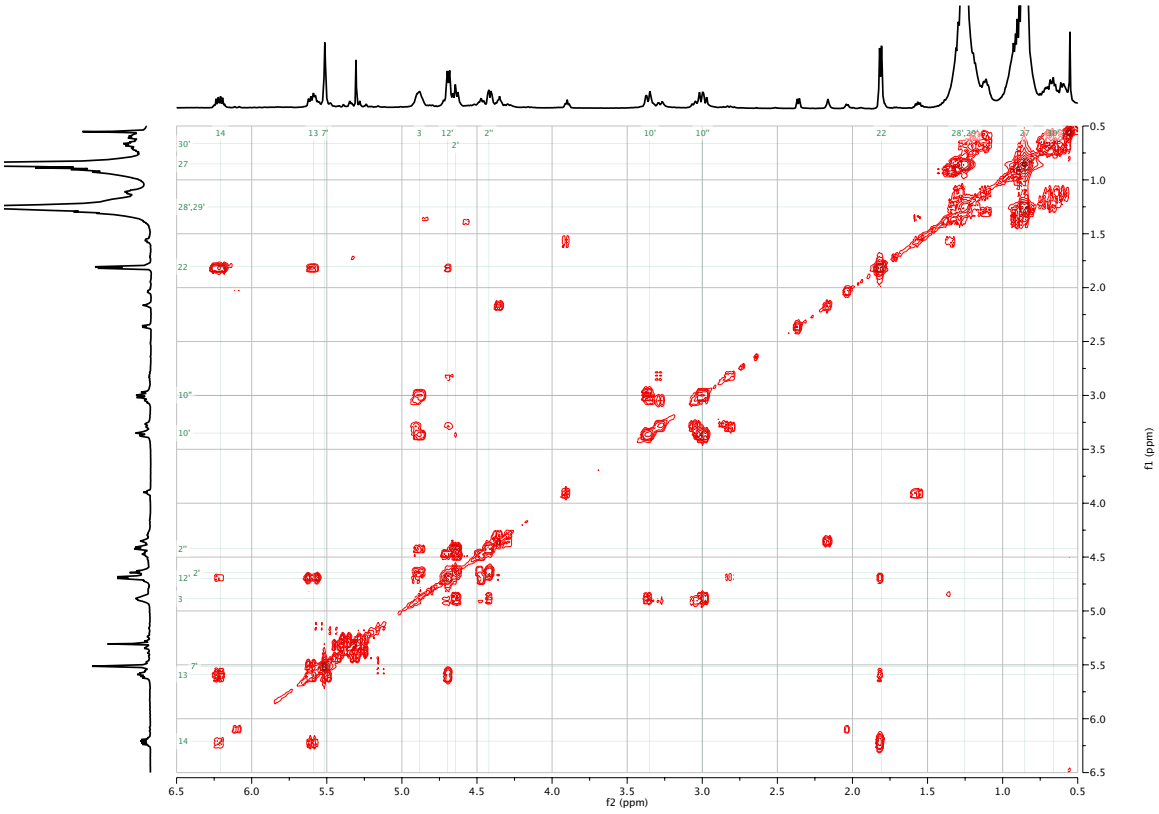
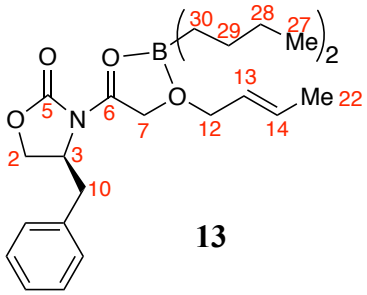


Figure A.3.8. COSY spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	gHMBCAD
4	Number of Scans	2
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.3000



13

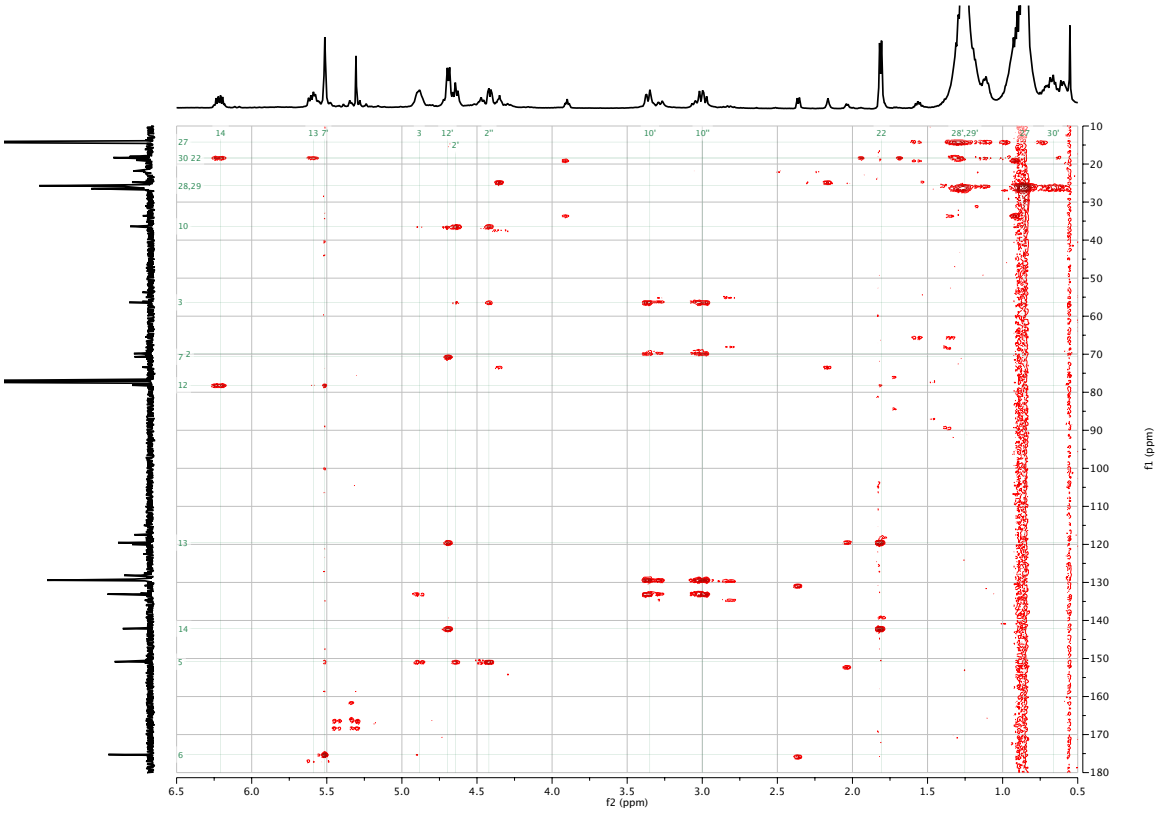
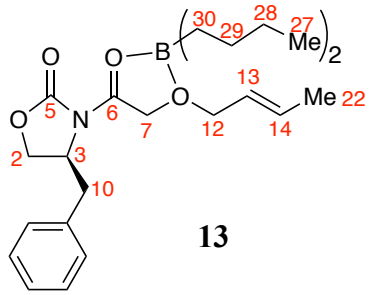


Figure A.3.9. HMBC spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-30.0
3	Pulse Sequence	ROESYAD
4	Number of Scans	4
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.4000



13

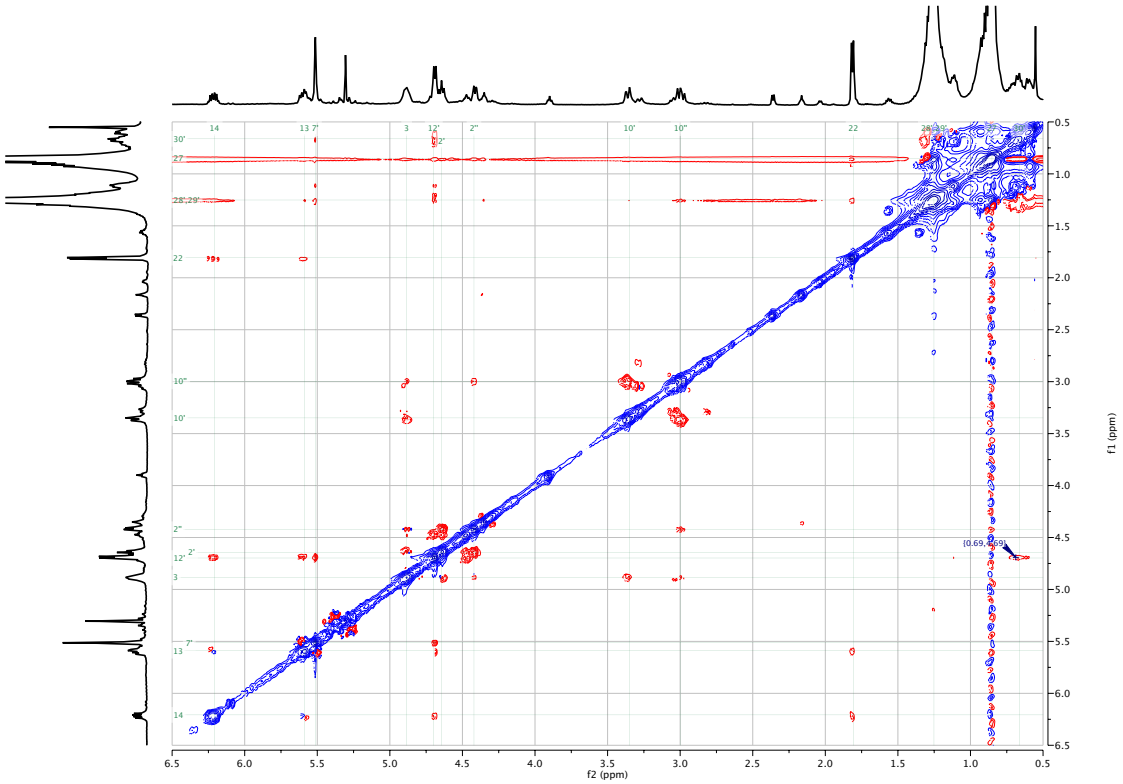
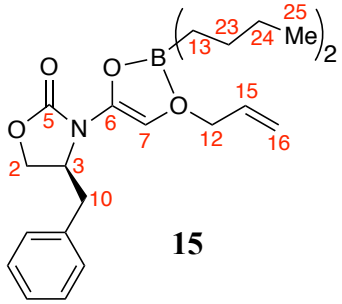


Figure A.3.10. ROESY spectrum of 0.20 M **13** in $CDCl_3$ recorded at –30 ºC.



15

Table A.3.2. ^{1}H and ^{13}C chemical shift assignments for **15**.[a, b]

Atom #	δ ^{13}C, ppm	δ ^{1}H, ppm	COSY	HMBC	ROESY
2	70.0	4.39 (2')	2"		
		4.30 (2")	2', 3		
3	58.5	4.39	2", 10', 10"	5	10', 10", 7
10	37.9	3.05 (10')	10", 3	3, 2	3
		2.98 (10")	10', 3		3
7	124.8	5.78		12	12, 3
12	75.5	4.30	15, 16', 16"	7, 15, 16	13, 7, 15, 16'
15	135.9	5.95	12, 16', 16"	12	13, 12, 16', 16"
16	120.1	5.35 (16')	12, 15, 16"	15, 12	12, 15
		5.25 (16")	12, 15, 16'		15
13	22.6	0.50	23	23	12, 15, 23
23, 24	28.5	1.24	13, 25	25, 13	13, 25
25	16.4	0.86	24	24	24
5	159.8				
6	172.0				

[a] Important correlations that allowed determination of subunit arrangement are marked in red. [b] *n*-butyl groups time average.

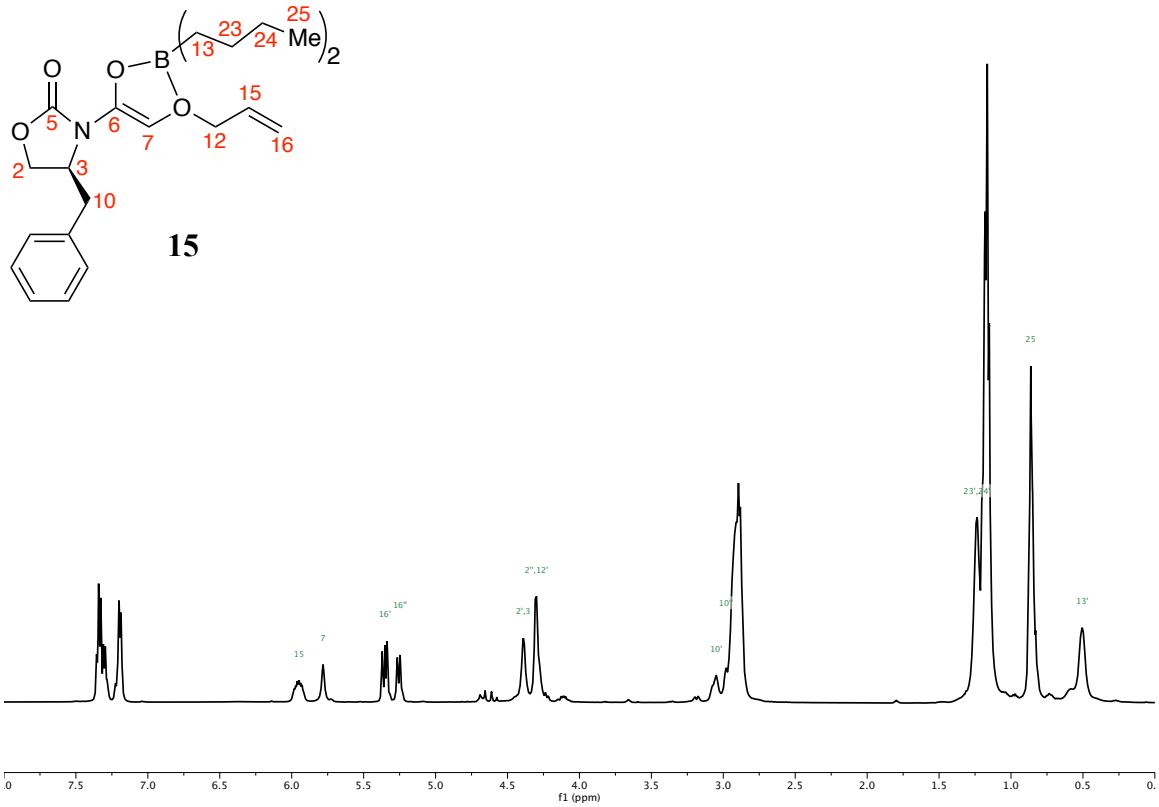


Figure A.3.11. ^{1}H NMR spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

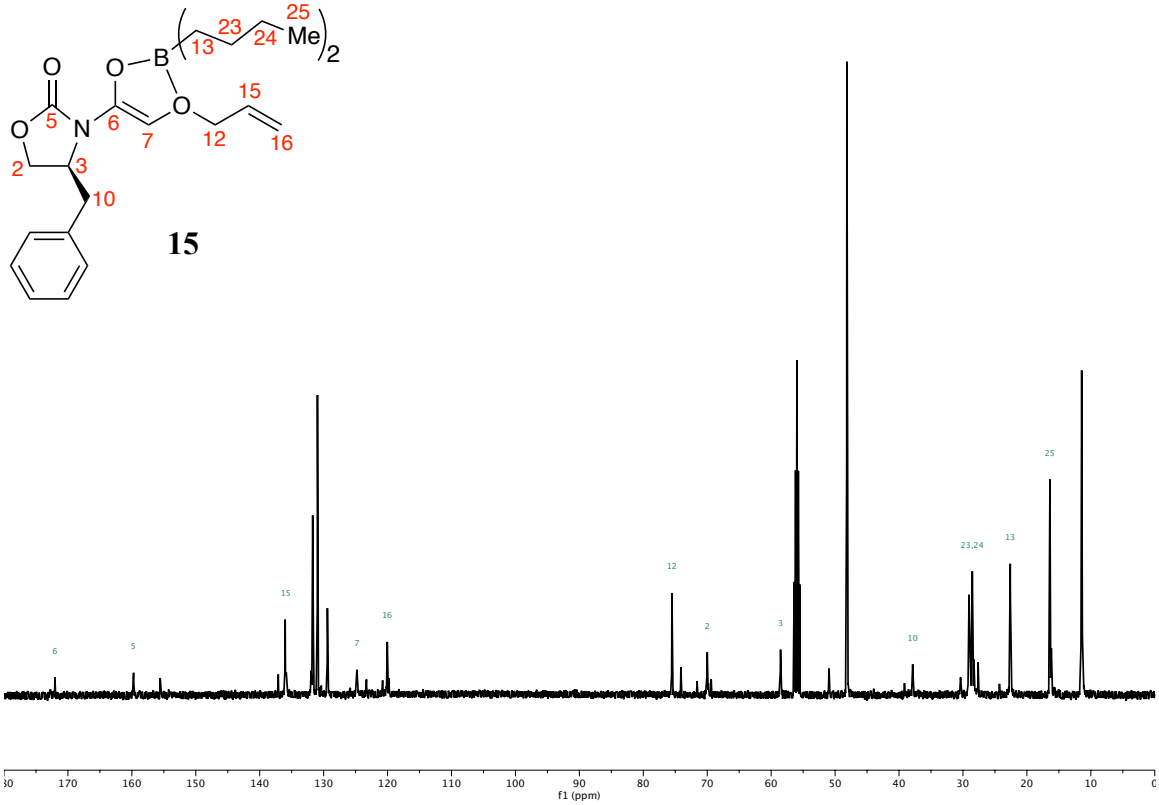
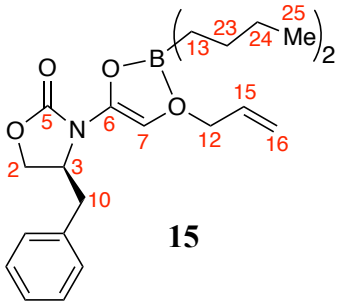


Figure A.3.12. $^{13}C\{^{1}H\}$ NMR spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC. Extra peaks are rearranged product alkoxide.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	HSQCAD
4	Number of Scans	2
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.1501



15

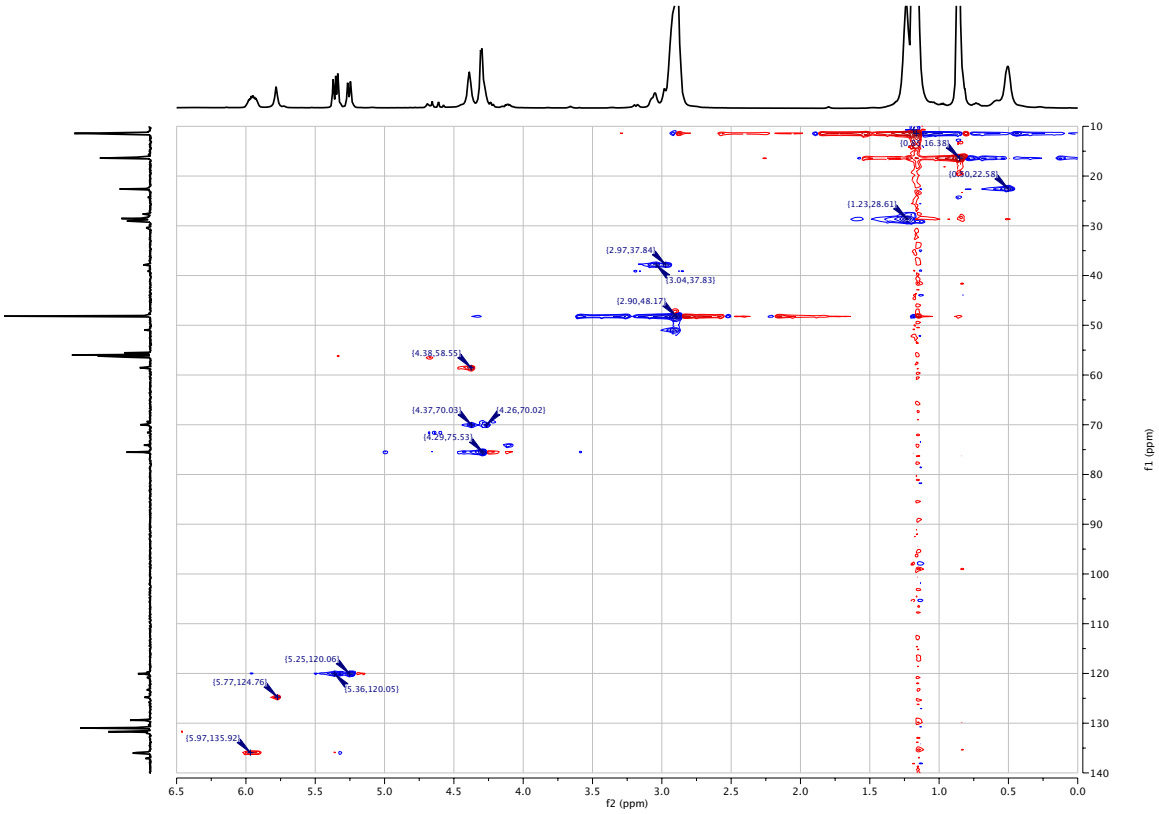
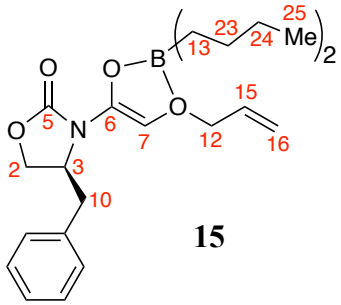


Figure A.3.13. HSQC spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	gCOSY
4	Number of Scans	1
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.5000



15

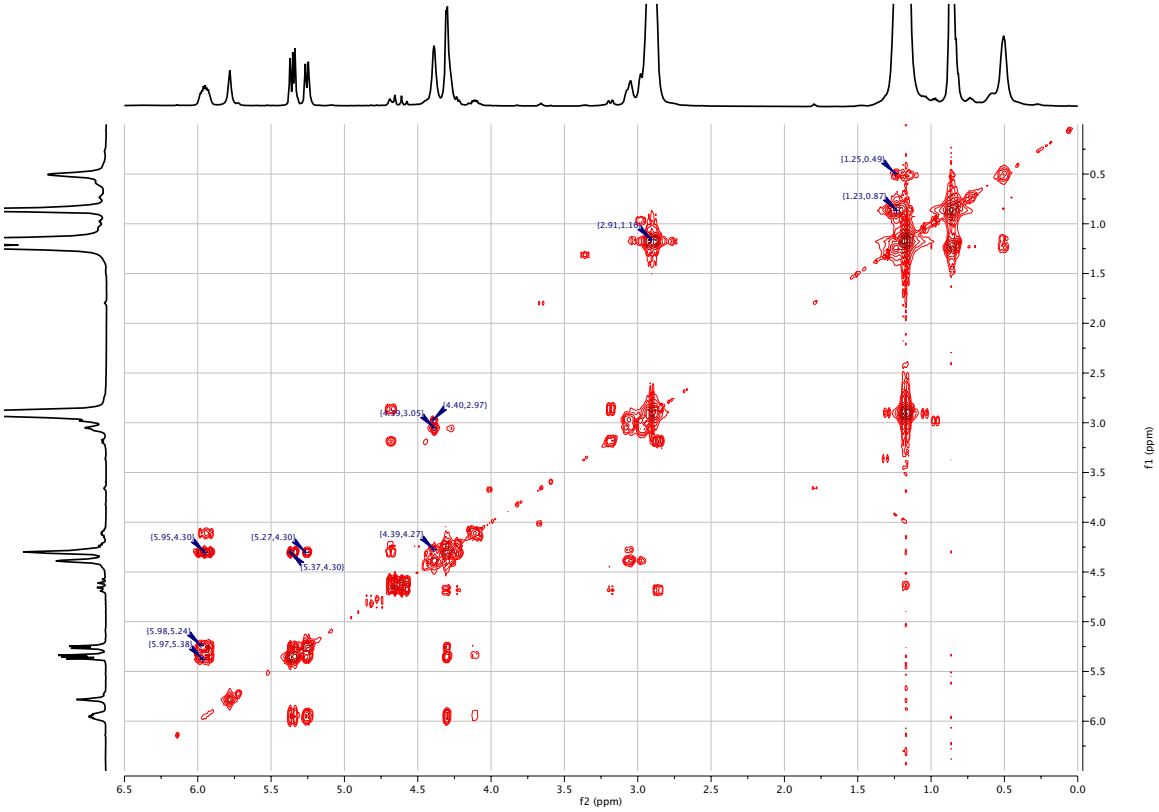
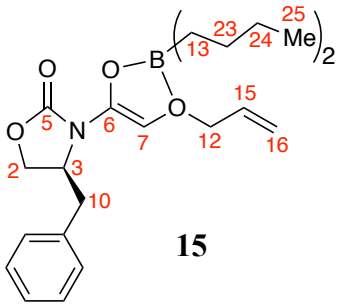


Figure A.3.14. COSY spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	-50.0
3	Pulse Sequence	gHMBCAD
4	Number of Scans	2
5	Receiver Gain	10
6	Relaxation Delay	1.0000
7	Pulse Width	8.5000
8	Acquisition Time	0.3000



15

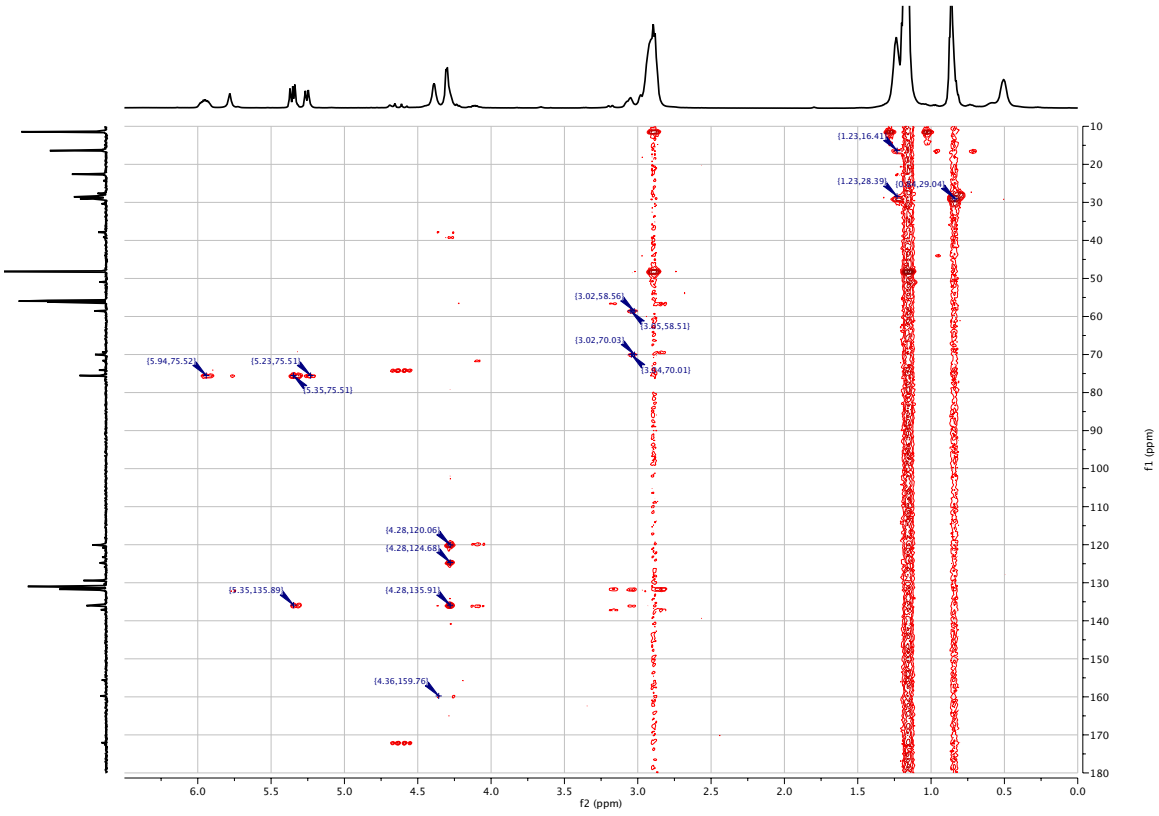
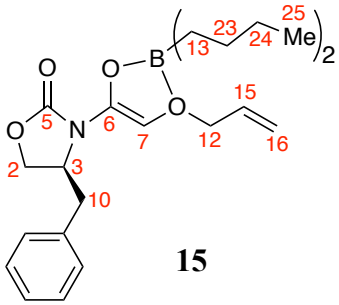


Figure A.3.15. HMBC spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

Parameter	Value
1 Solvent	cdcl3
2 Temperature	-50.0
3 Pulse Sequence	ROESYAD
4 Number of Scans	4
5 Receiver Gain	10
6 Relaxation Delay	1.0000
7 Pulse Width	8.5000
8 Acquisition Time	0.4000



15

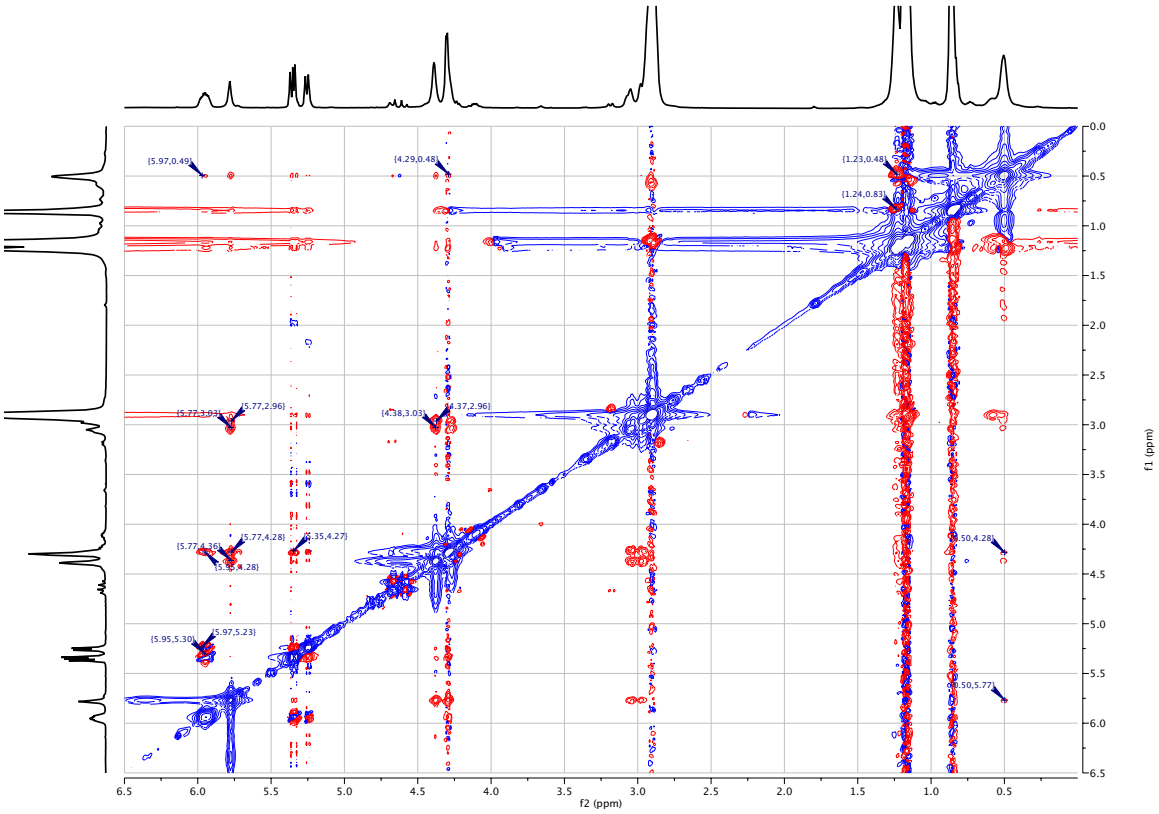


Figure A.3.16. ROESY spectrum of 0.20 M **15** in $CDCl_3$ recorded at –50 ºC.

3. Kinetics

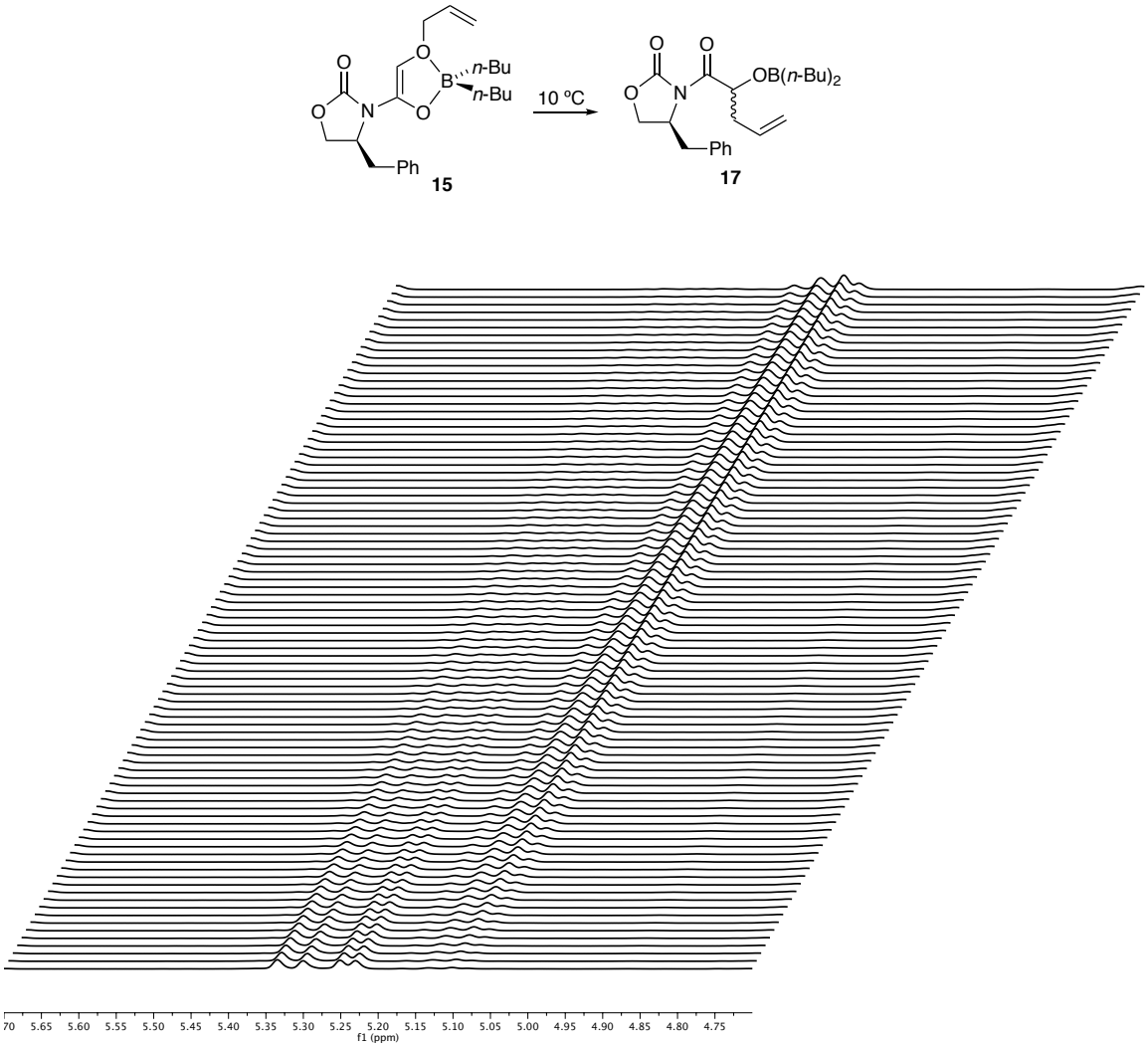


Figure A.3.17. ^{1}H NMR spectra recorded at 10 ºC following the rearrangement of **15** generated in a solution of 0.10 M **1a**, 0.11 M *n*-Bu_2BOTf, and 0.12 M Et_3N in $CDCl_3$. The decay and growth correspond to with the allyl protons of **15** and product alkoxide **17**, respectively.

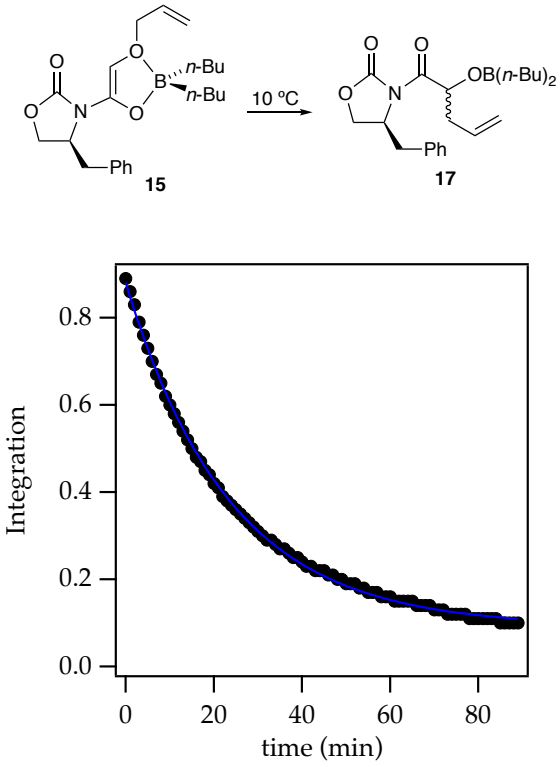


Figure A.3.18. Plot following the loss of **15** at 10 ºC in a solution generated from 0.10 M **1a**, 0.11 M *n*-Bu_2BOTf, and 0.12 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.788 \pm 0.003$, $b = 0.0427 \pm 0.0004$, $c = 0.092 \pm 0.002$. The curvature fits a first-order decay.

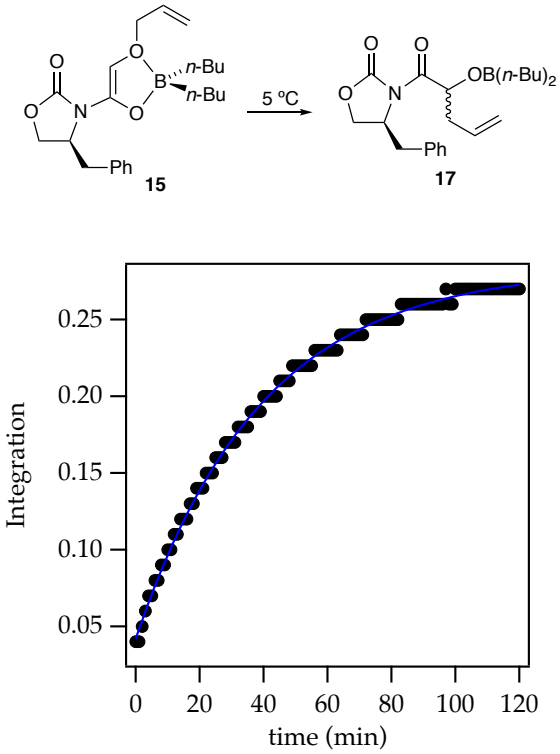


Figure A.3.19. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 0.10 M *n*-Bu_2BOTf, and 0.10 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.242 \pm 0.001$, $b = 0.0255 \pm 0.0003$, $c = 0.042 \pm 0.001$. The curvature fits a first order growth.

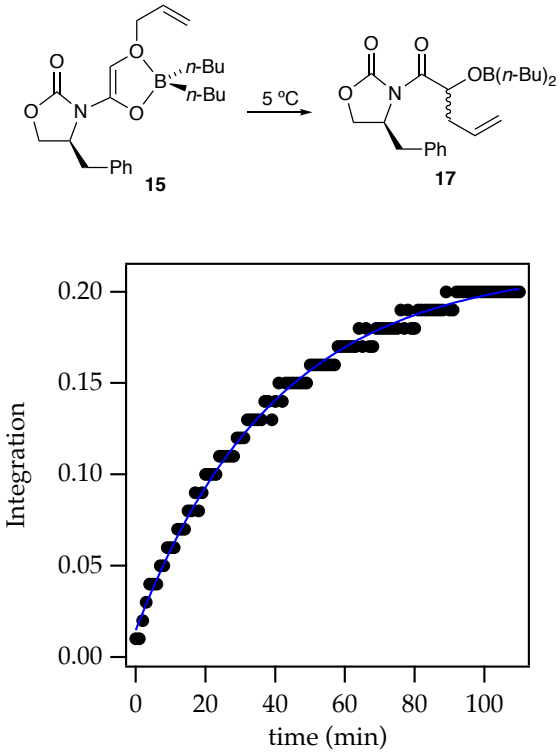


Figure A.3.20. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 0.10 M *n*-Bu_2BOTf, and 1.0 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.200 \pm 0.001$, $b = 0.0249 \pm 0.0005$, $c = 0.015 \pm 0.001$. k_{obsd} is the same (within 10%) as using 1.0 equiv of Et_3N, confirming no dependence on amine concentration.

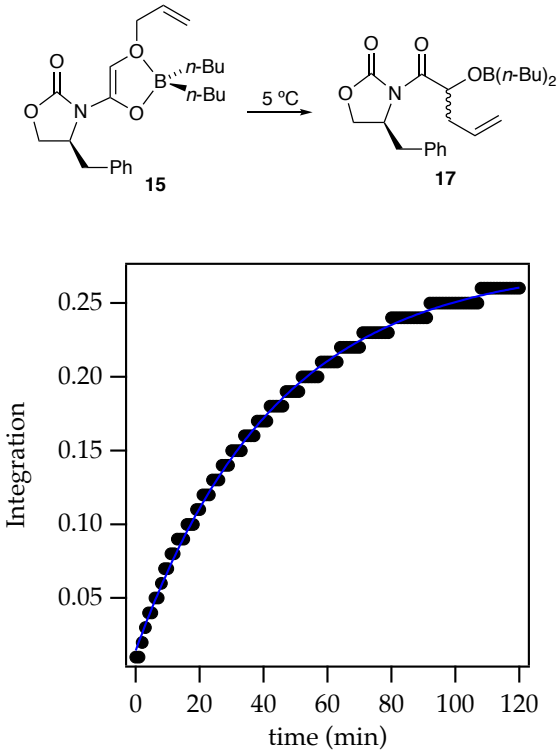


Figure A.3.21. Plot following the rearrangement of **15** at 5 ºC generated from 0.10 M **1a**, 1.0 M *n*-Bu_2BOTf, and 1.0 M Et_3N in $CDCl_3$. The curve depicts a least-squares fit to $y = ae^{-bx}+c$, such that $a = 0.263 \pm 0.001$, $b = 0.0229 \pm 0.0003$, $c = 0.015 \pm 0.001$. k_{obsd} is the same (within 10%) as using 1.0 equiv of *n*-Bu_2BOTf, confirming no dependence on the *n*-Bu_2BOTf concentration.

4. Substrate synthesis

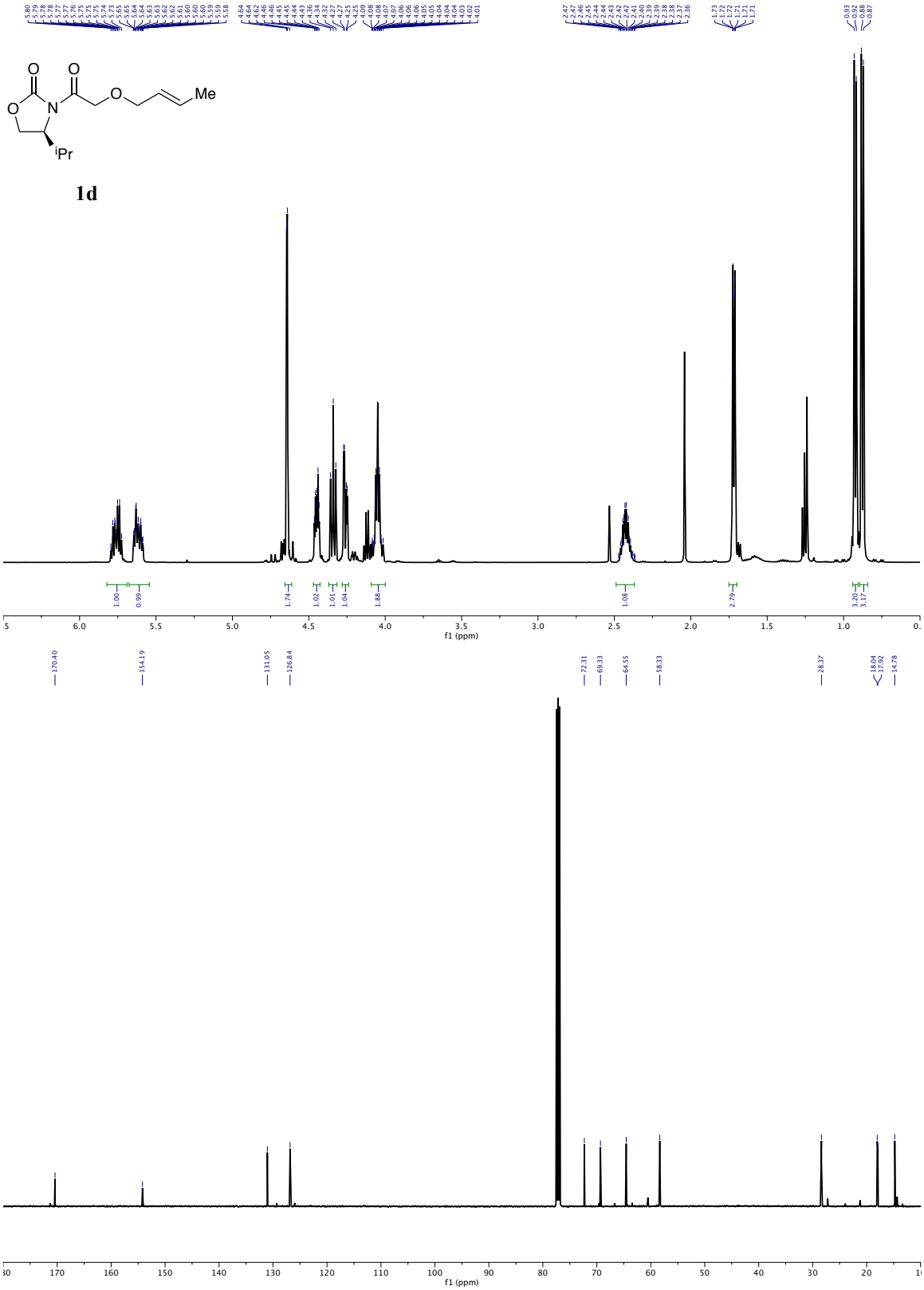


Figure A.3.22. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1d** in $CDCl_3$.

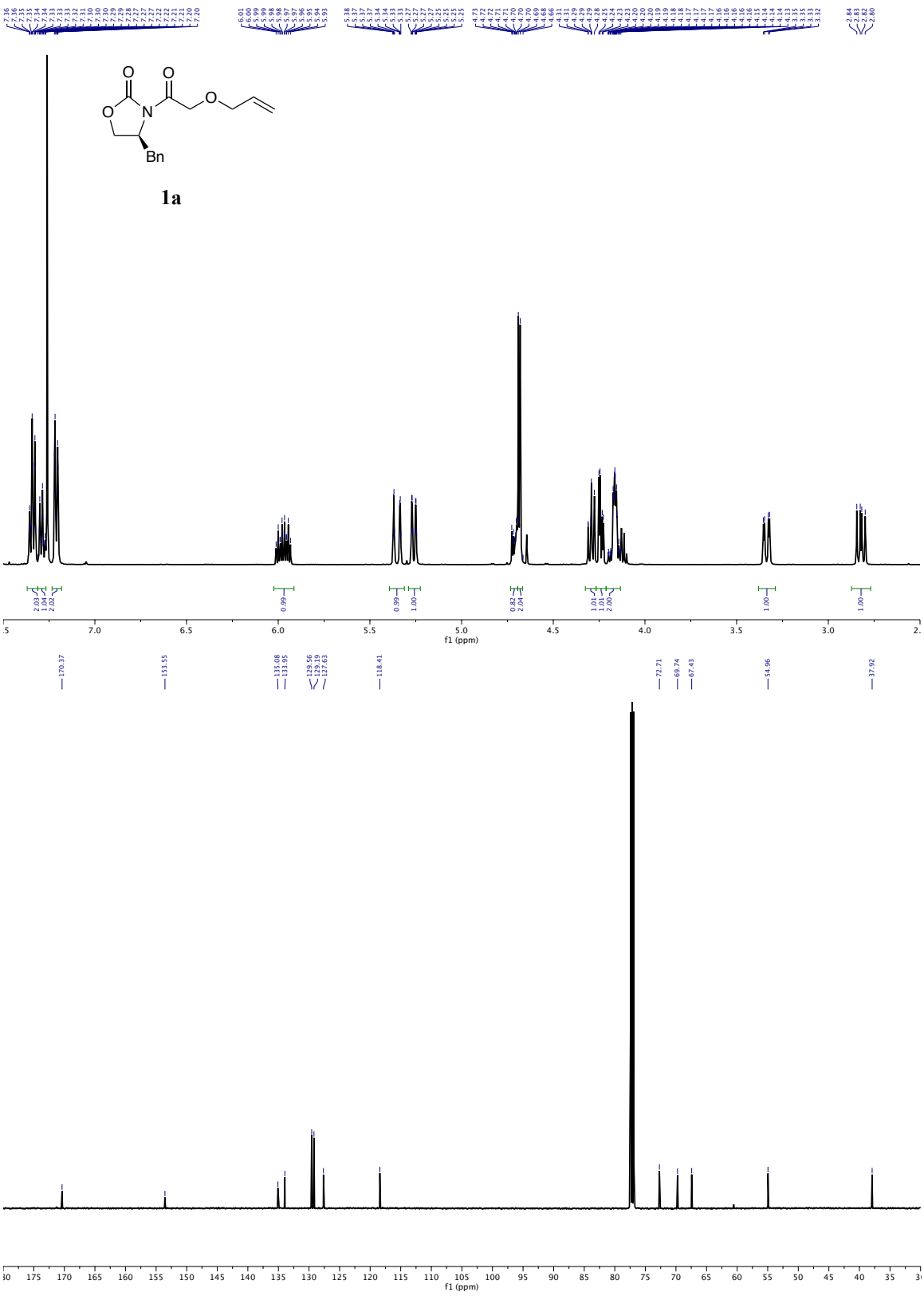


Figure A.3.23. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1a** in $CDCl_3$.

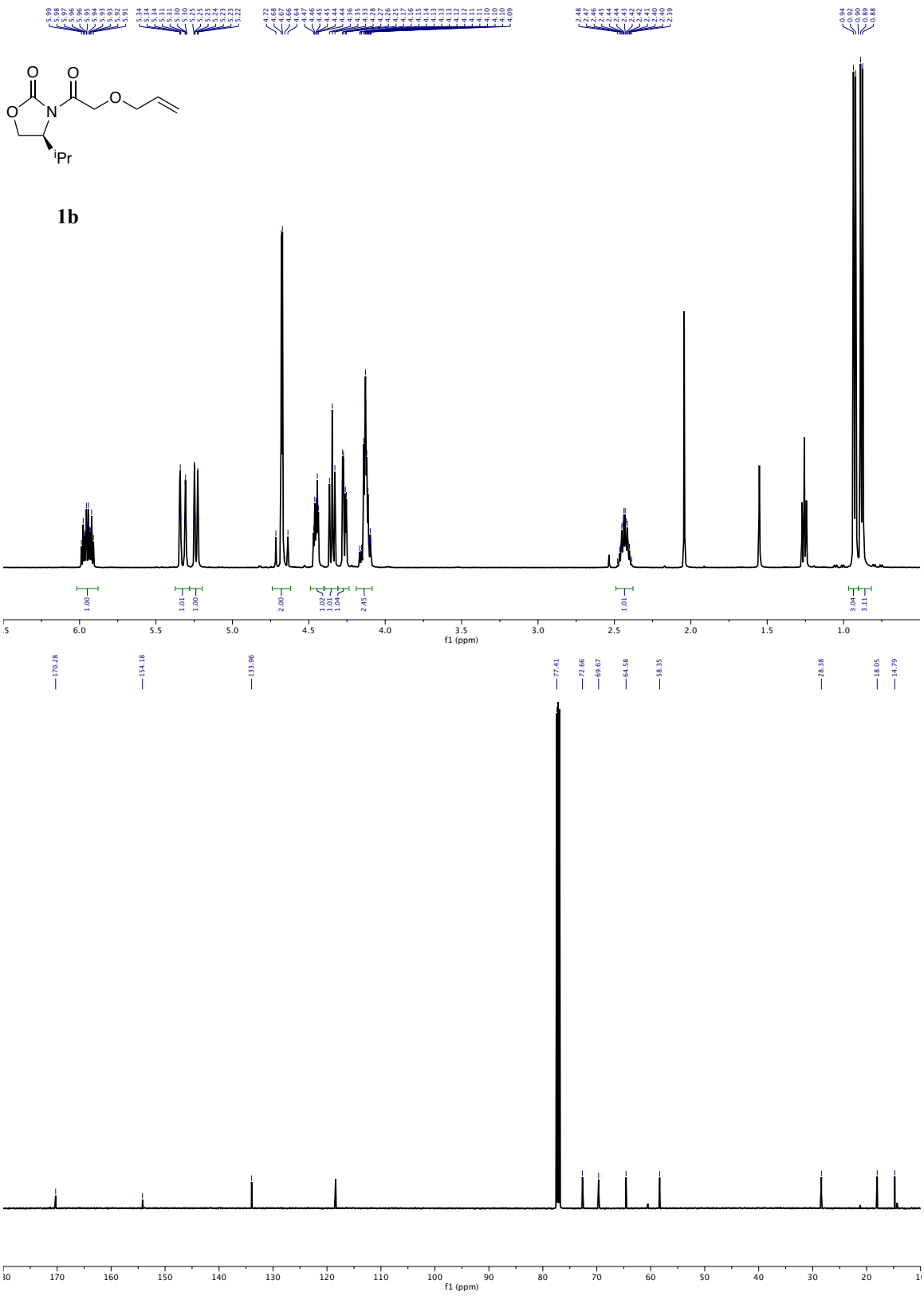


Figure A.3.24. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1b** in $CDCl_3$.

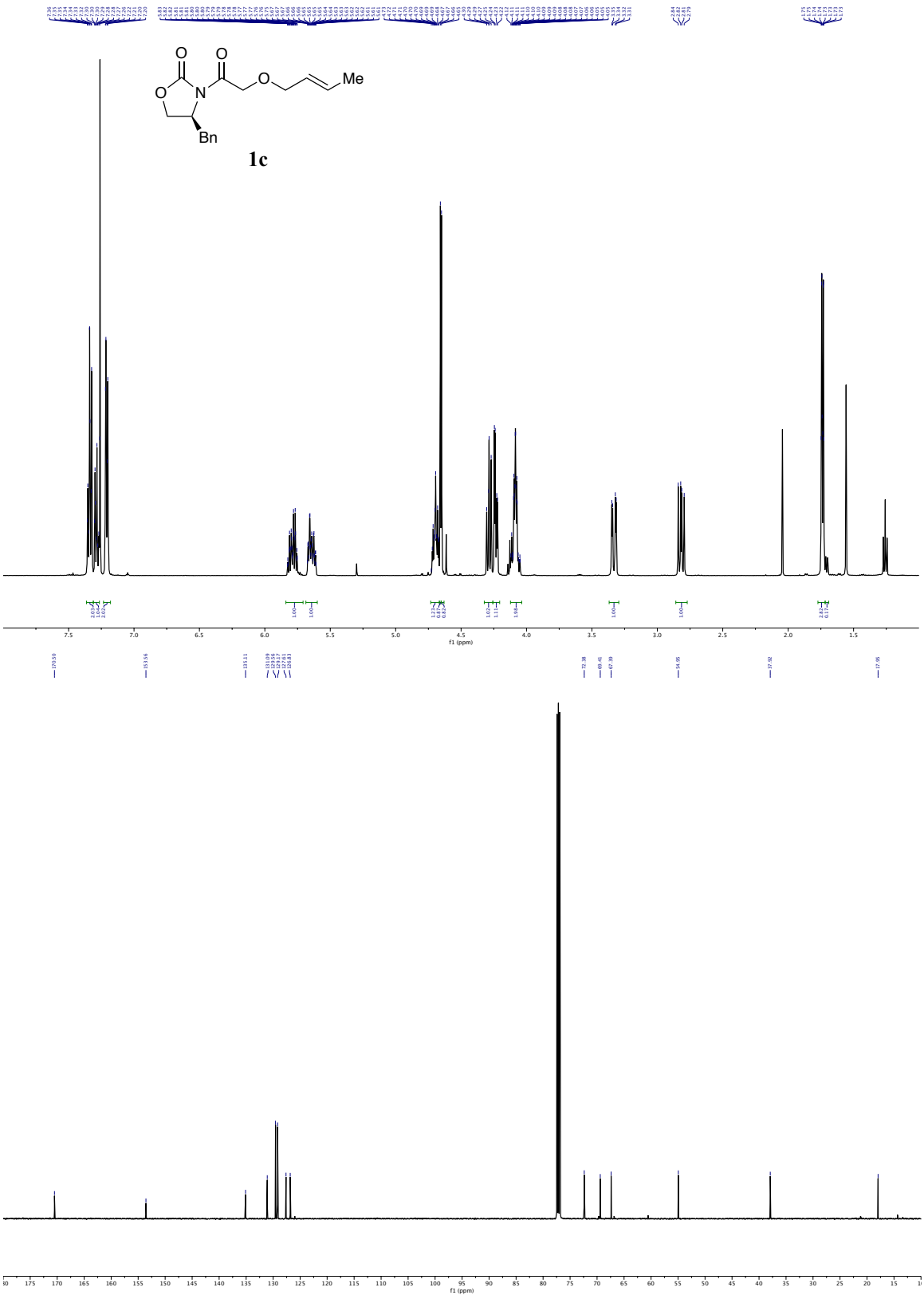


Figure A.3.25. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1c** in $CDCl_3$.

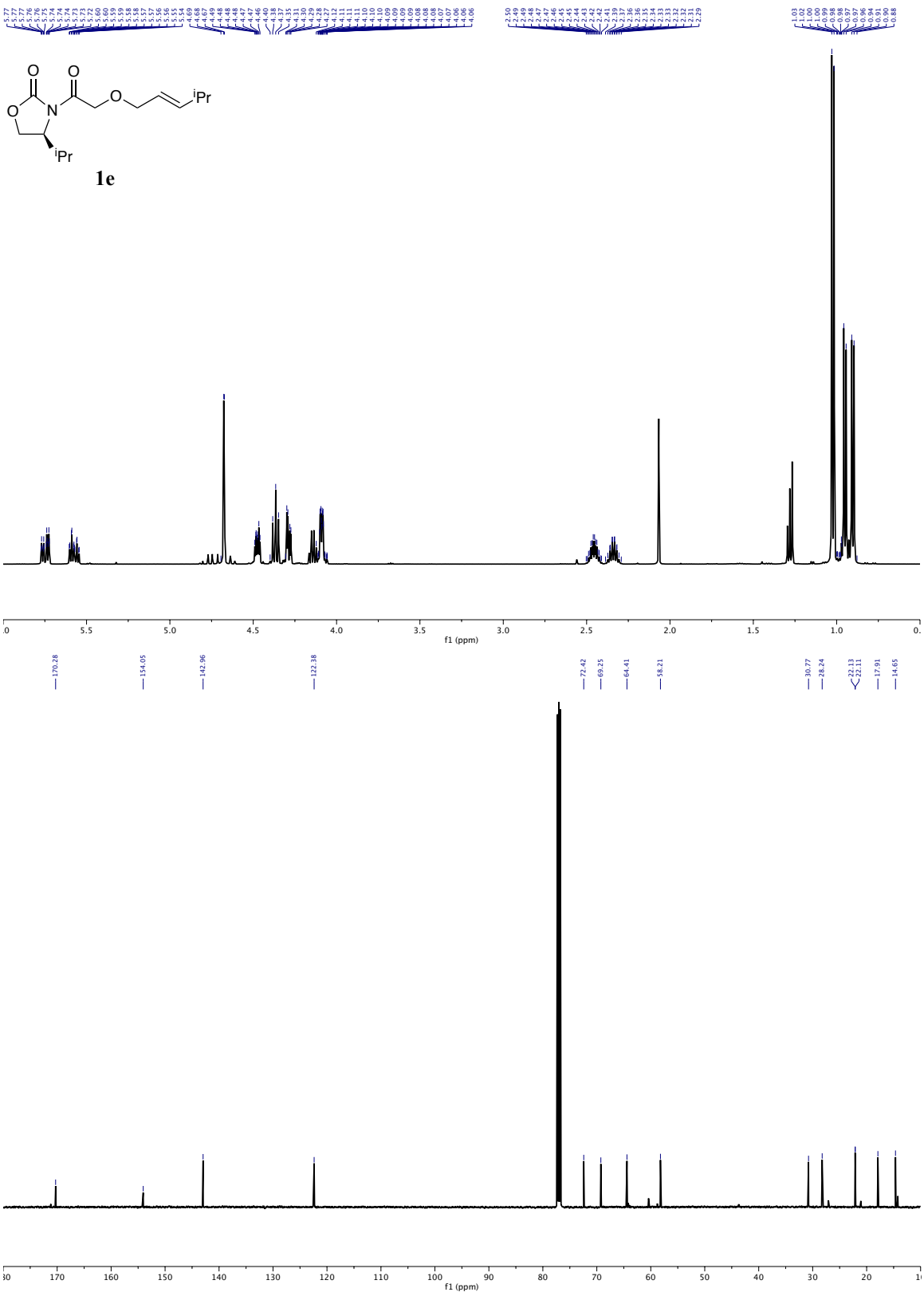


Figure A.3.26. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1e** in $CDCl_3$.

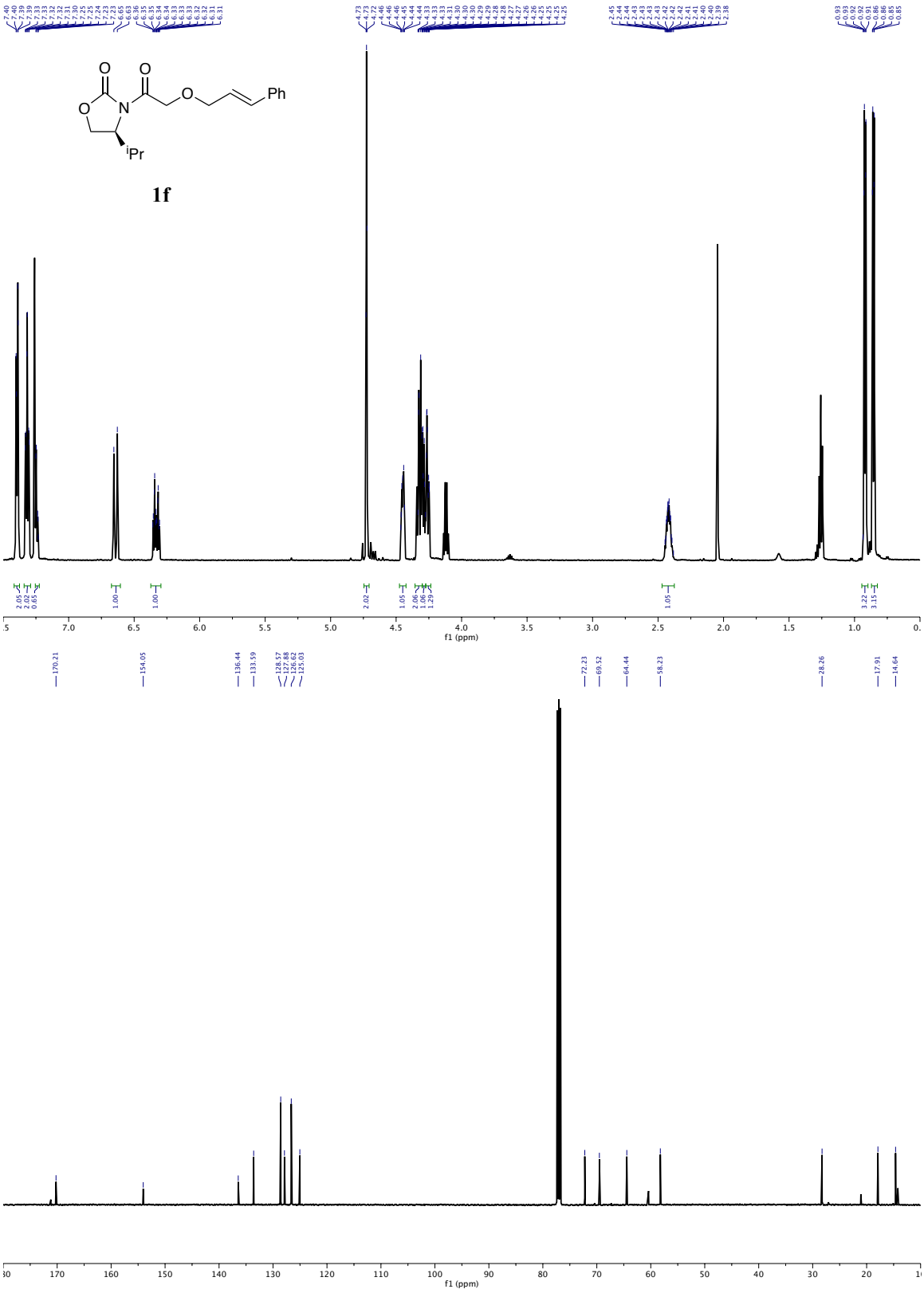


Figure A.3.27. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1f** in $CDCl_3$.

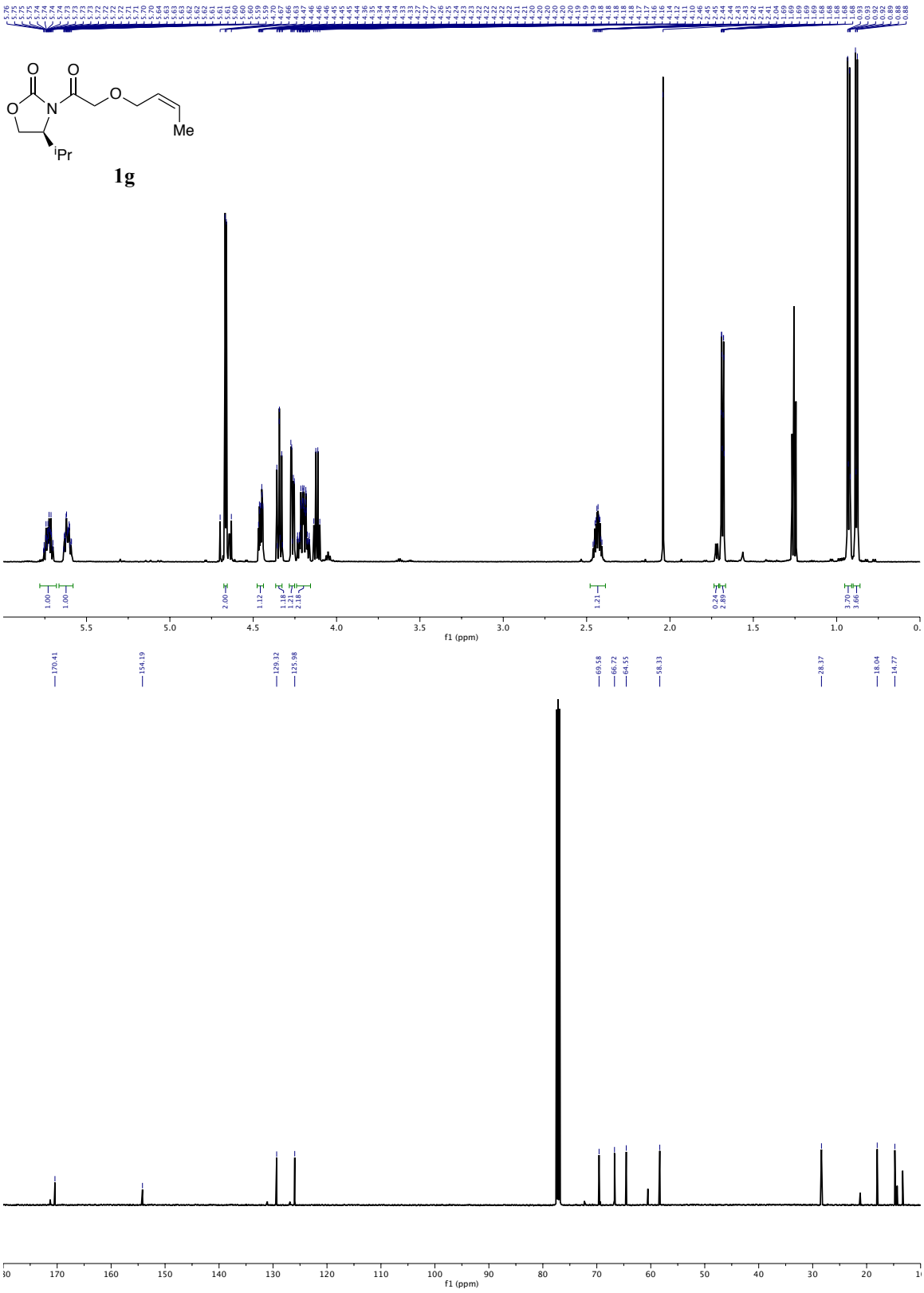


Figure A.3.28. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectrum of **1g** in $CDCl_3$.

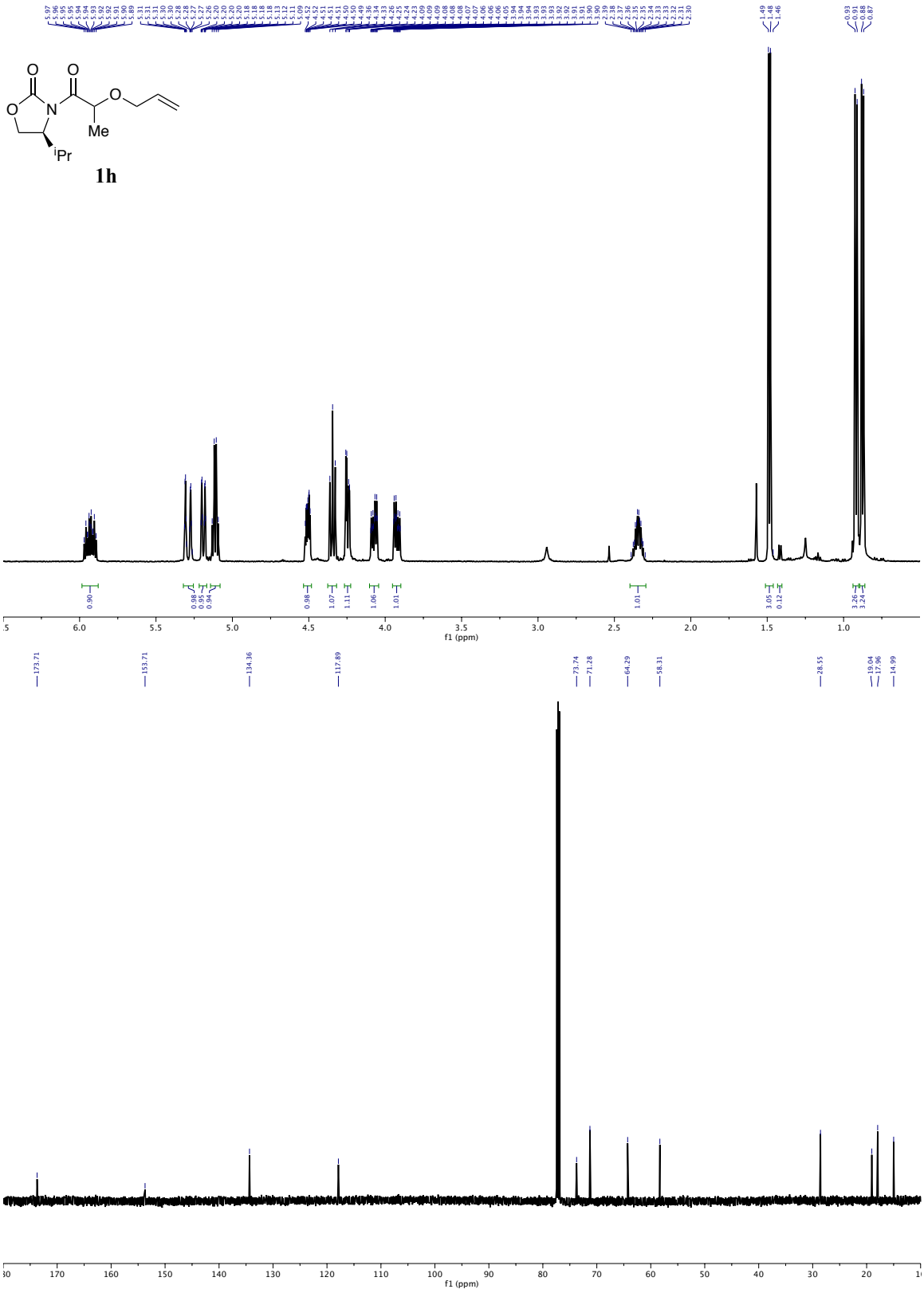


Figure A.3.29. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1h** in $CDCl_3$.

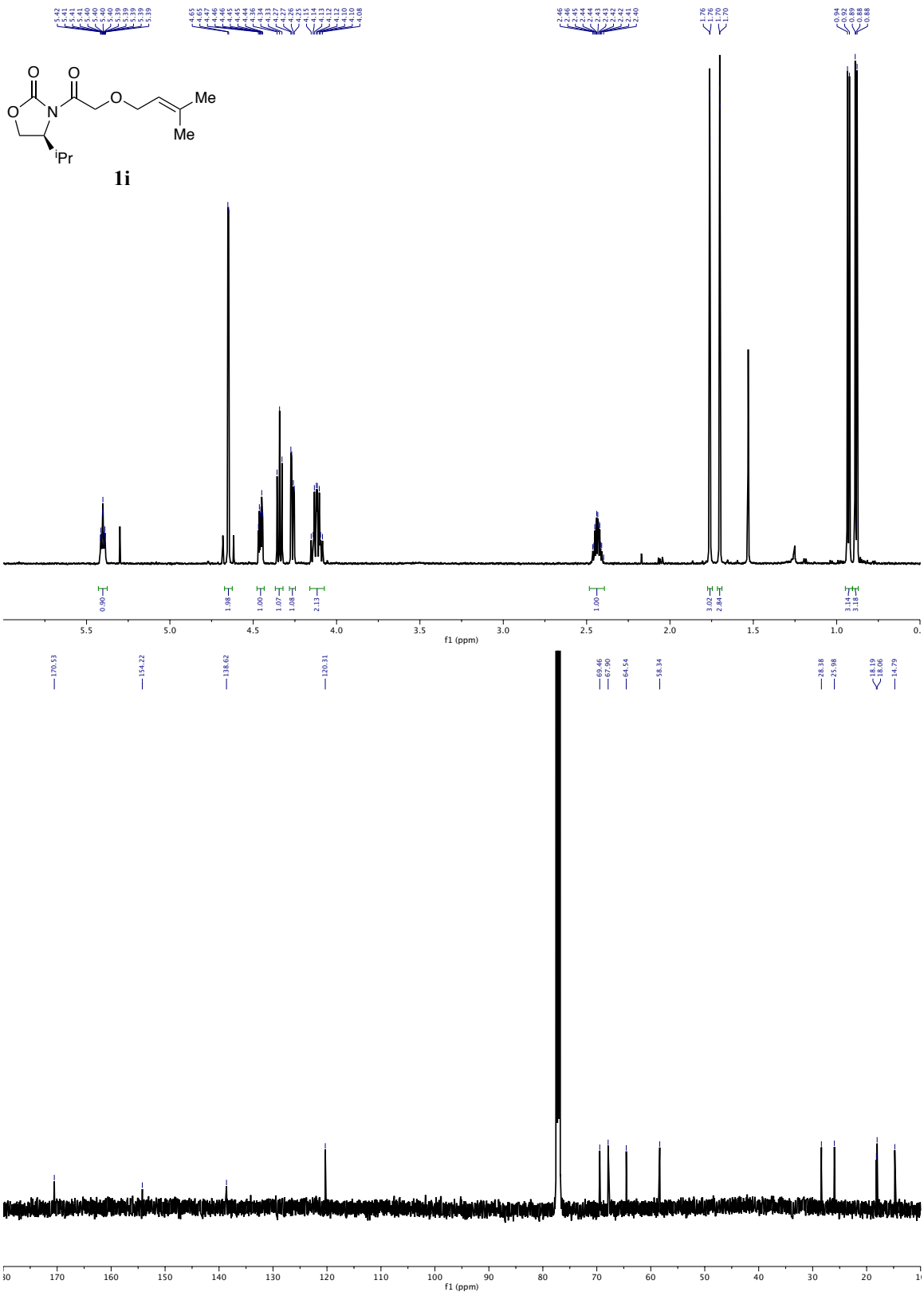


Figure A.3.30. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1i** in $CDCl_3$.

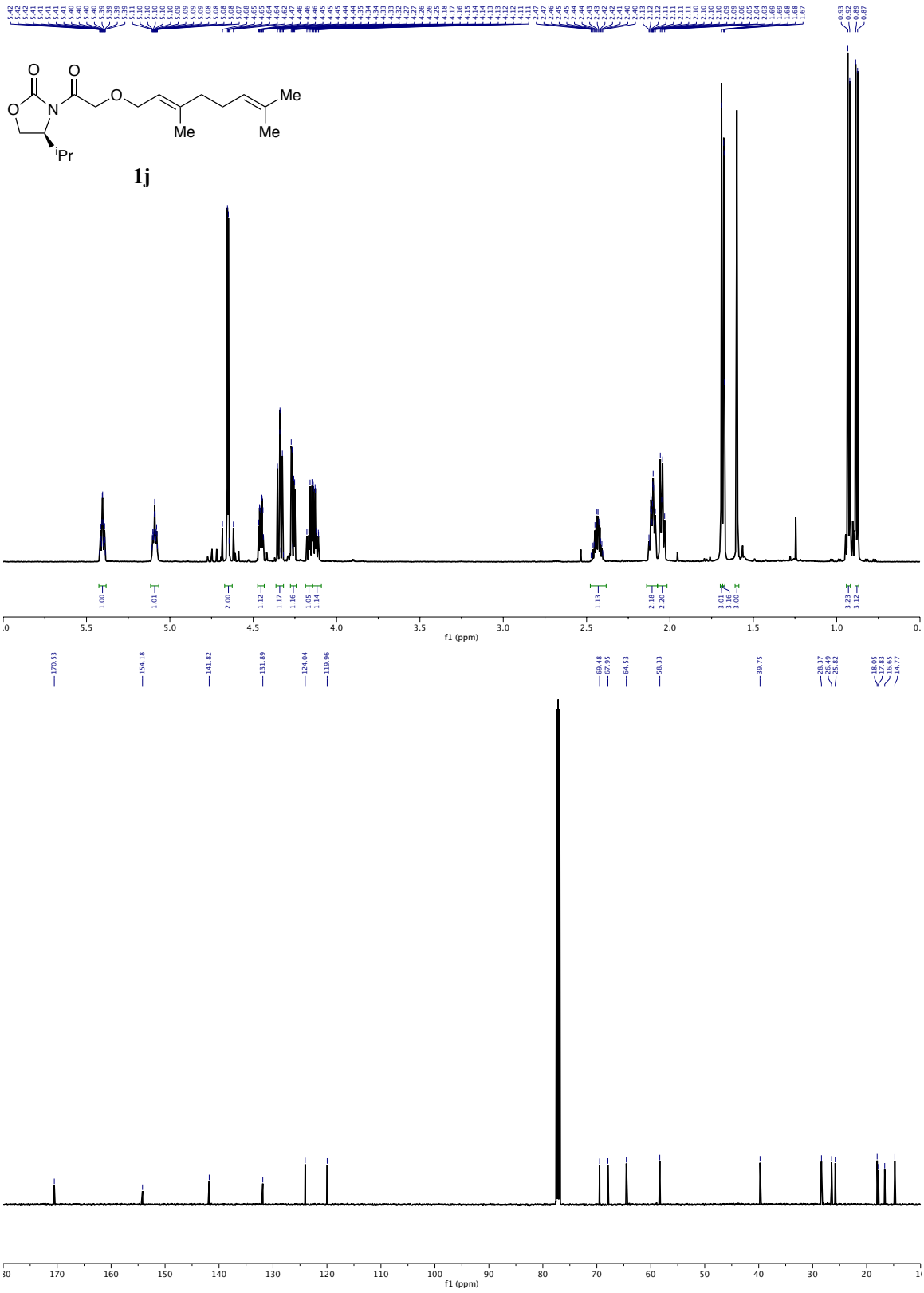


Figure A.3.31. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1j** in $CDCl_3$.

5. Rearrangements

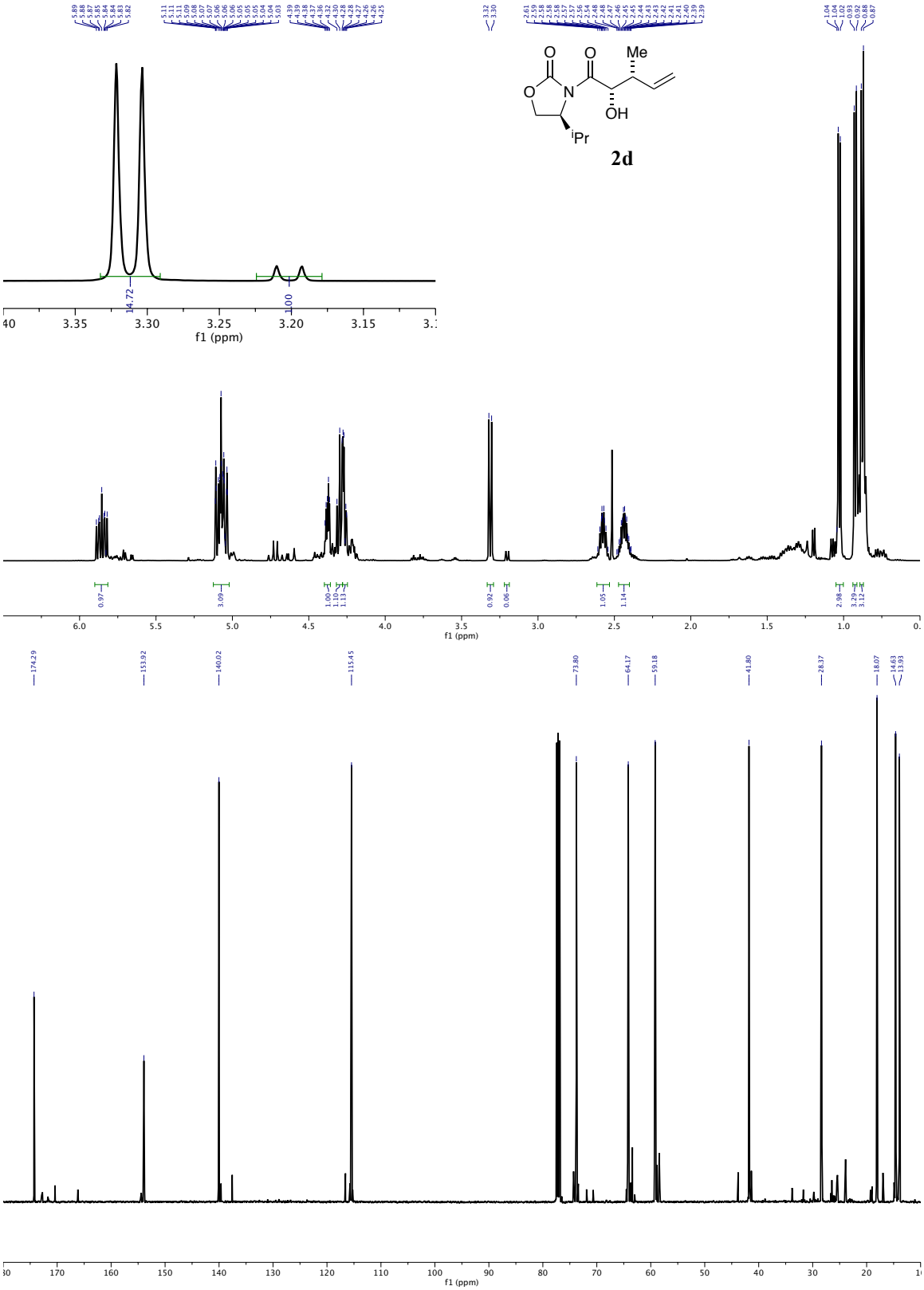


Figure A.3.32. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2d** in $CDCl_3$.

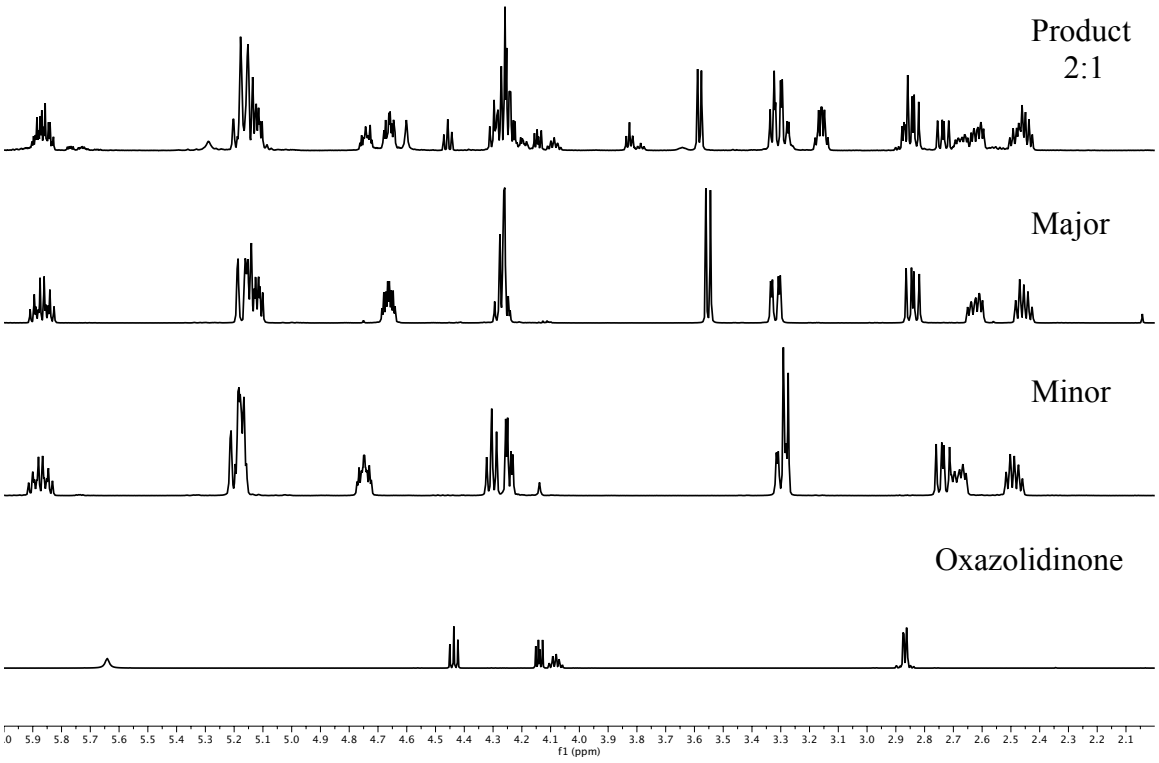


Figure A.3.33. ^{1}H NMR spectra of **2a** and its minor isomer in $CDCl_3$.

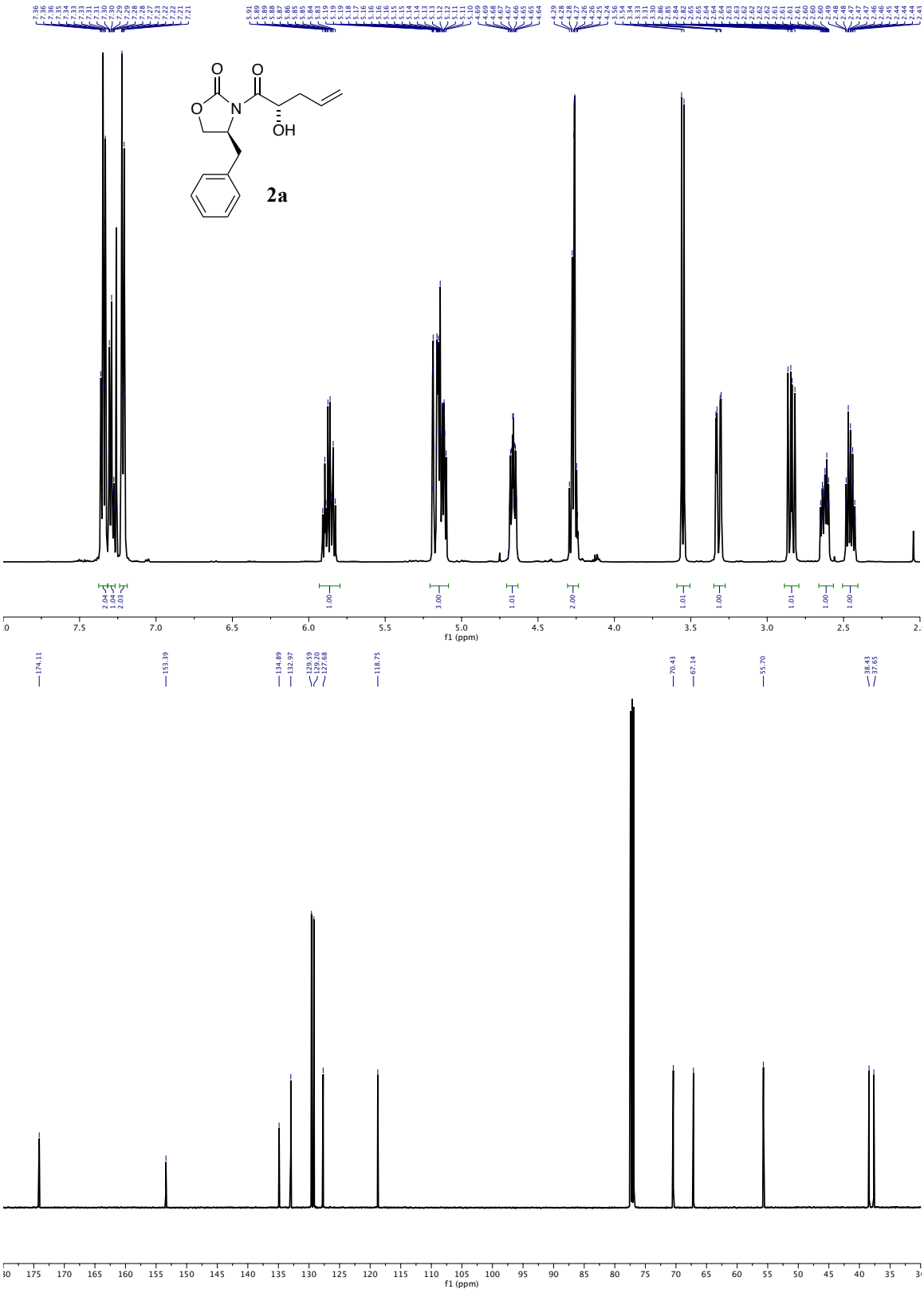


Figure A.3.34. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a** in $CDCl_3$.

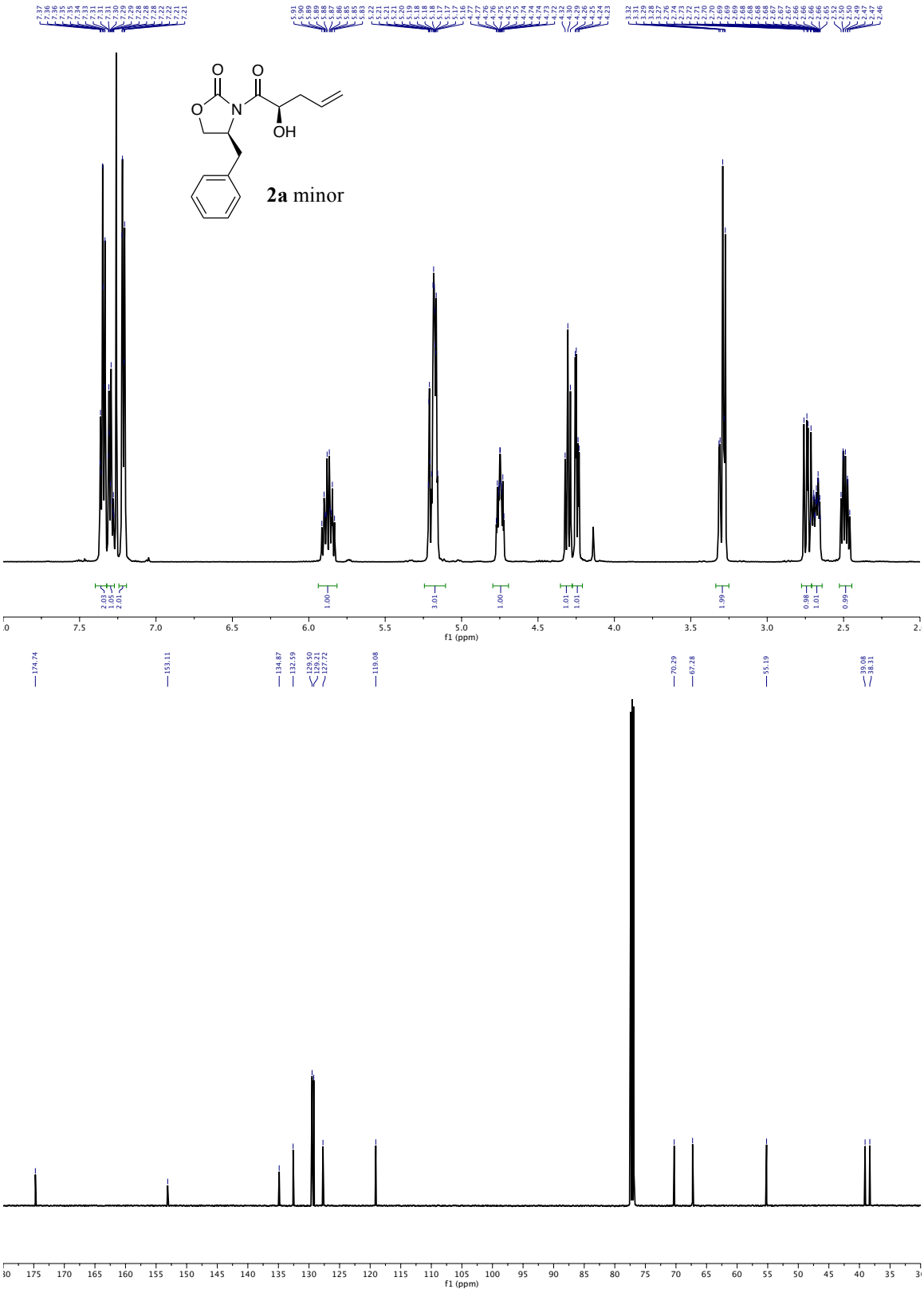


Figure A.3.35. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a** minor isomer in $CDCl_3$.

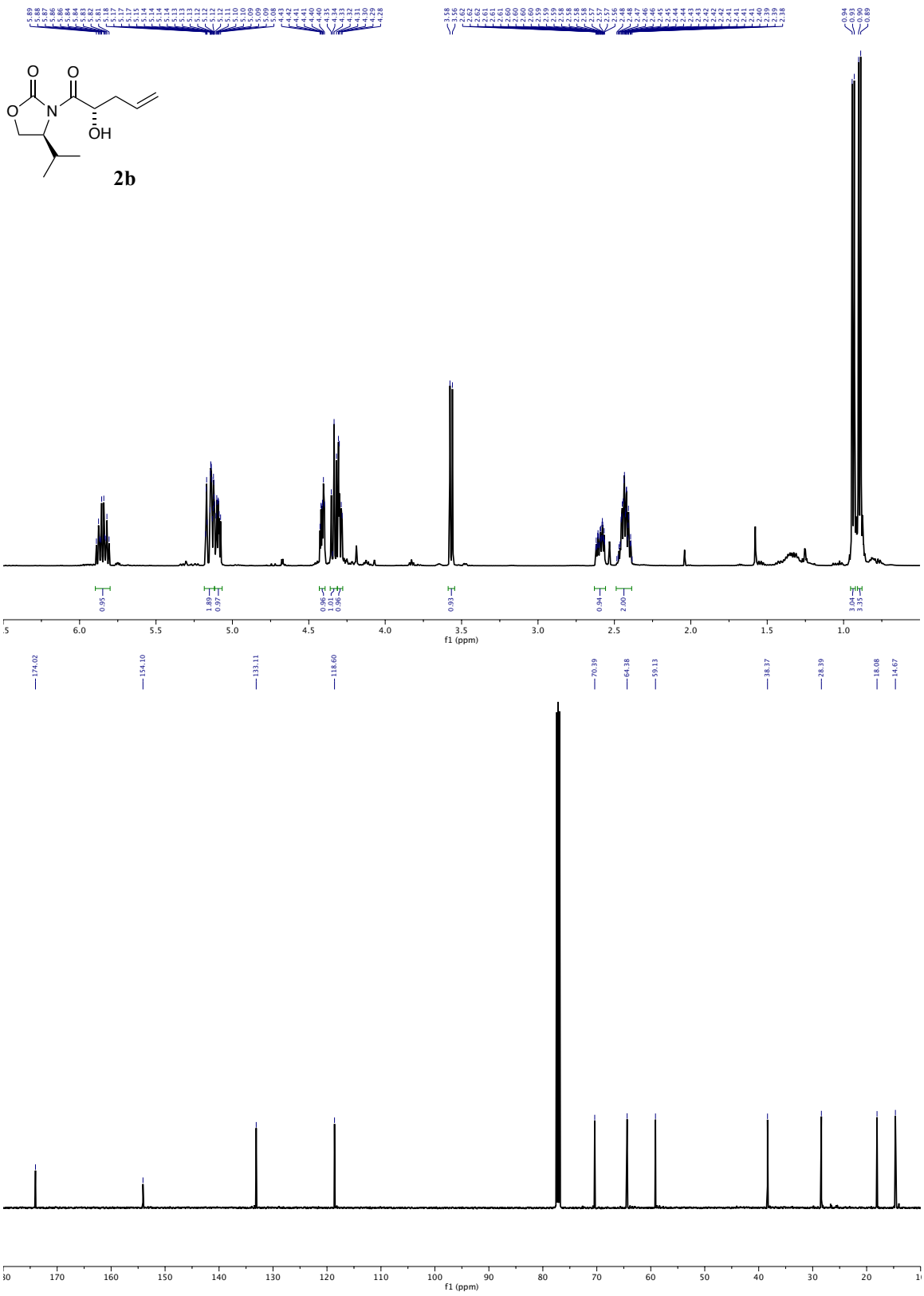


Figure A.3.36. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2b** in $CDCl_3$.

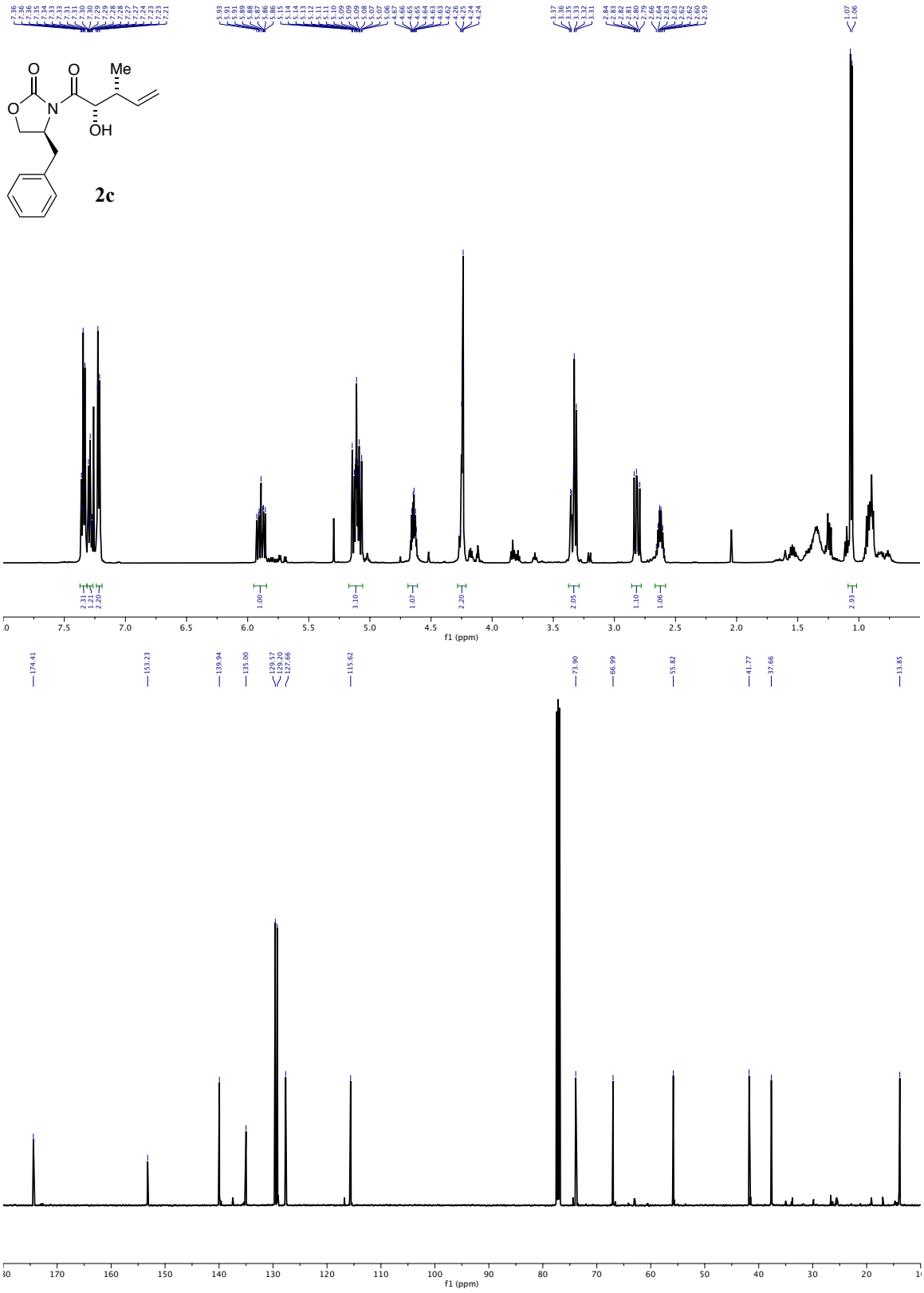


Figure A.3.37. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2c** in $CDCl_3$.

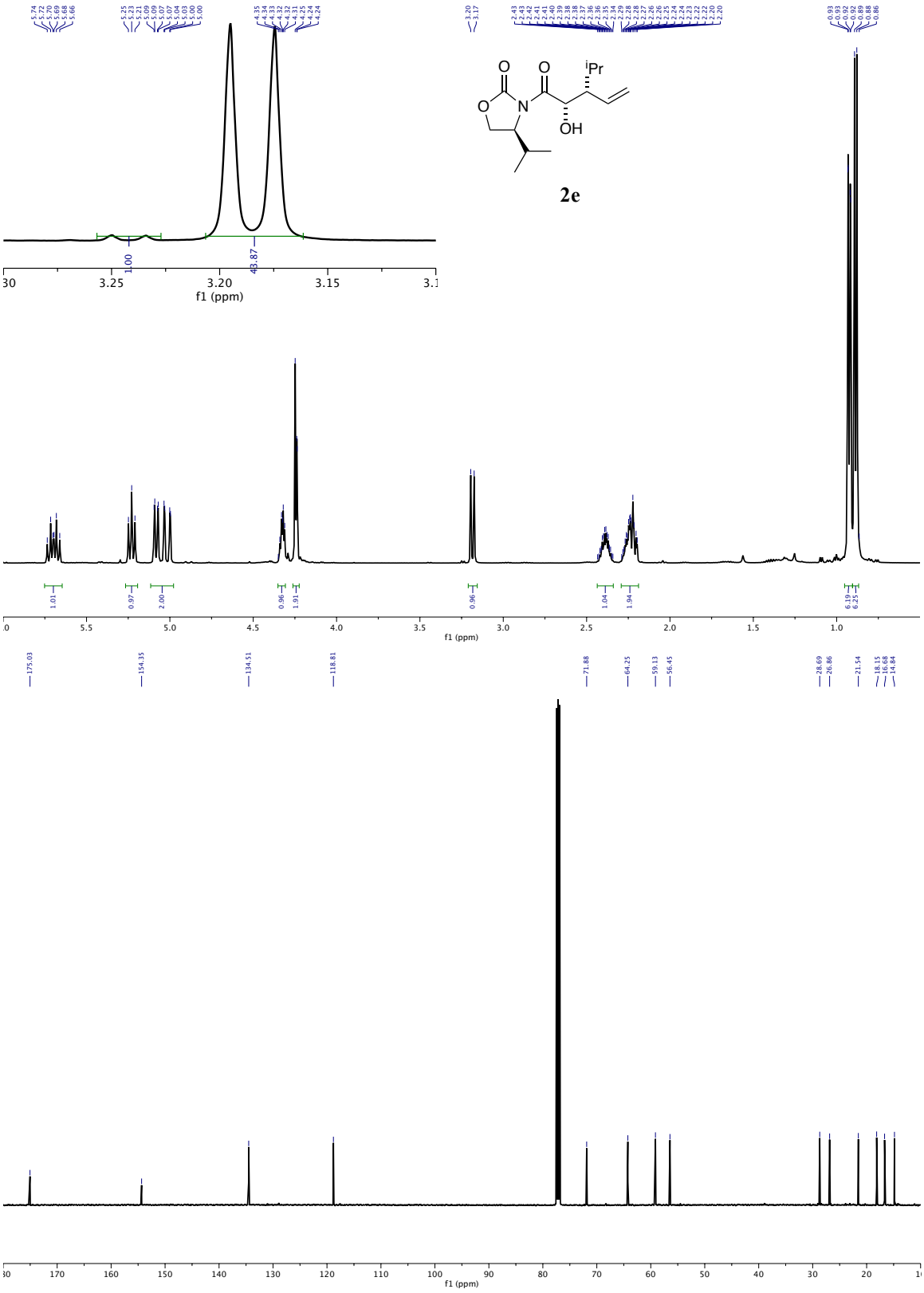
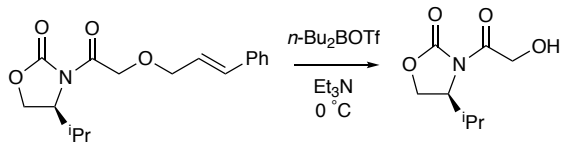


Figure A.3.38. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2e** in $CDCl_3$.



Decomposition of 1f. Following the procedure for **1d** except using **1f** afforded a decomposition product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (dt, *J* = 5.3, 1.8 Hz, 2H), 4.46 (dt, *J* = 8.5, 3.5 Hz, 1H), 4.38 (td, *J* = 8.8, 1.3 Hz, 1H), 4.30 (ddd, *J* = 9.2, 3.1, 1.3 Hz, 1H), 3.06 (td, *J* = 5.4, 1.3 Hz, 1H), 2.43 (dqd, *J* = 8.3, 7.1, 5.0 Hz, 1H), 0.95 (dd, *J* = 7.0, 1.4 Hz, 3H), 0.90 (dd, *J* = 6.9, 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.52, 153.81, 64.73, 63.25, 58.53, 28.43, 18.01, 14.76. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_8H_{13}NO_4$ 188.09173, found 188.09181.

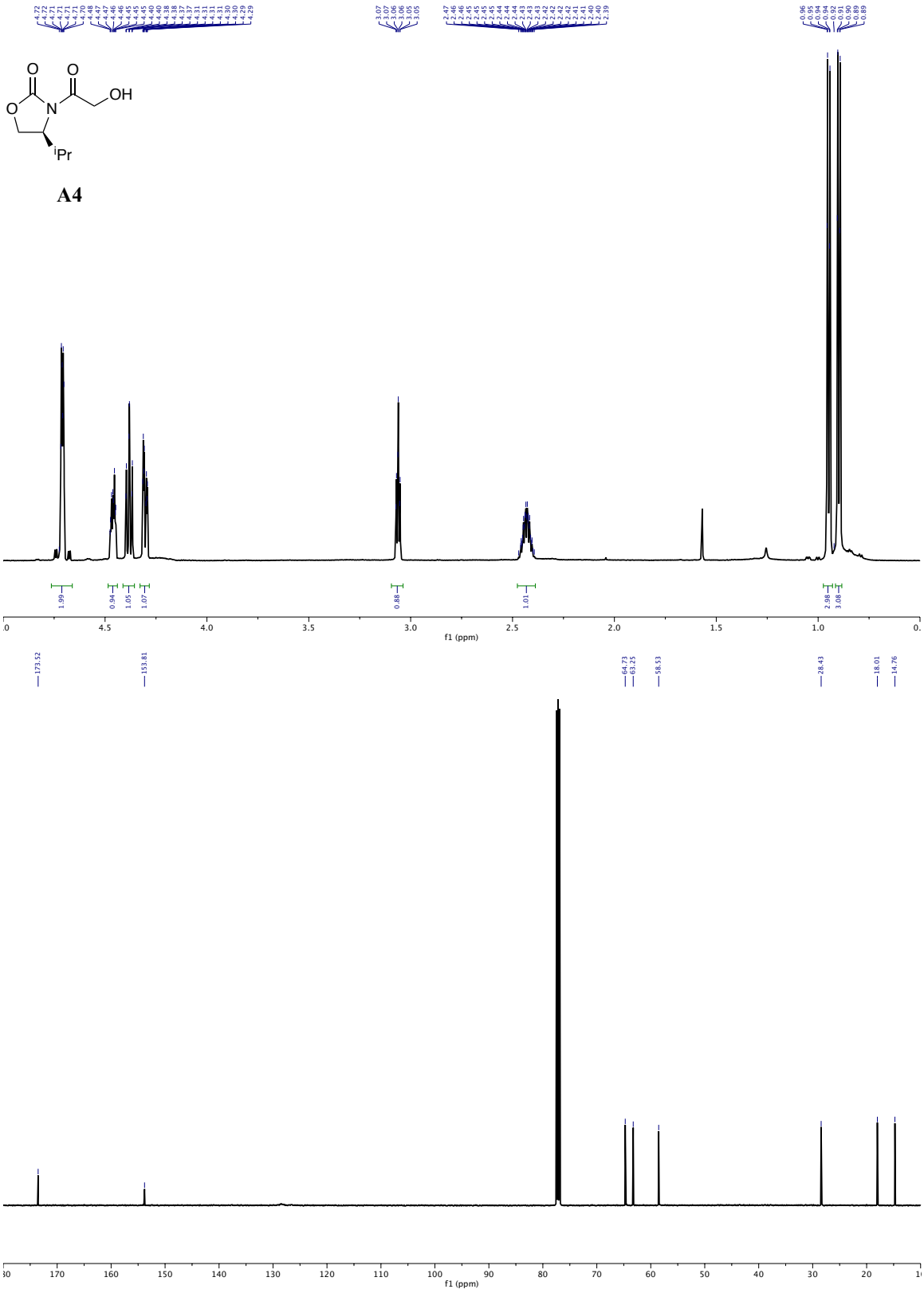


Figure A.3.39. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1f** decomposition in $CDCl_3$.

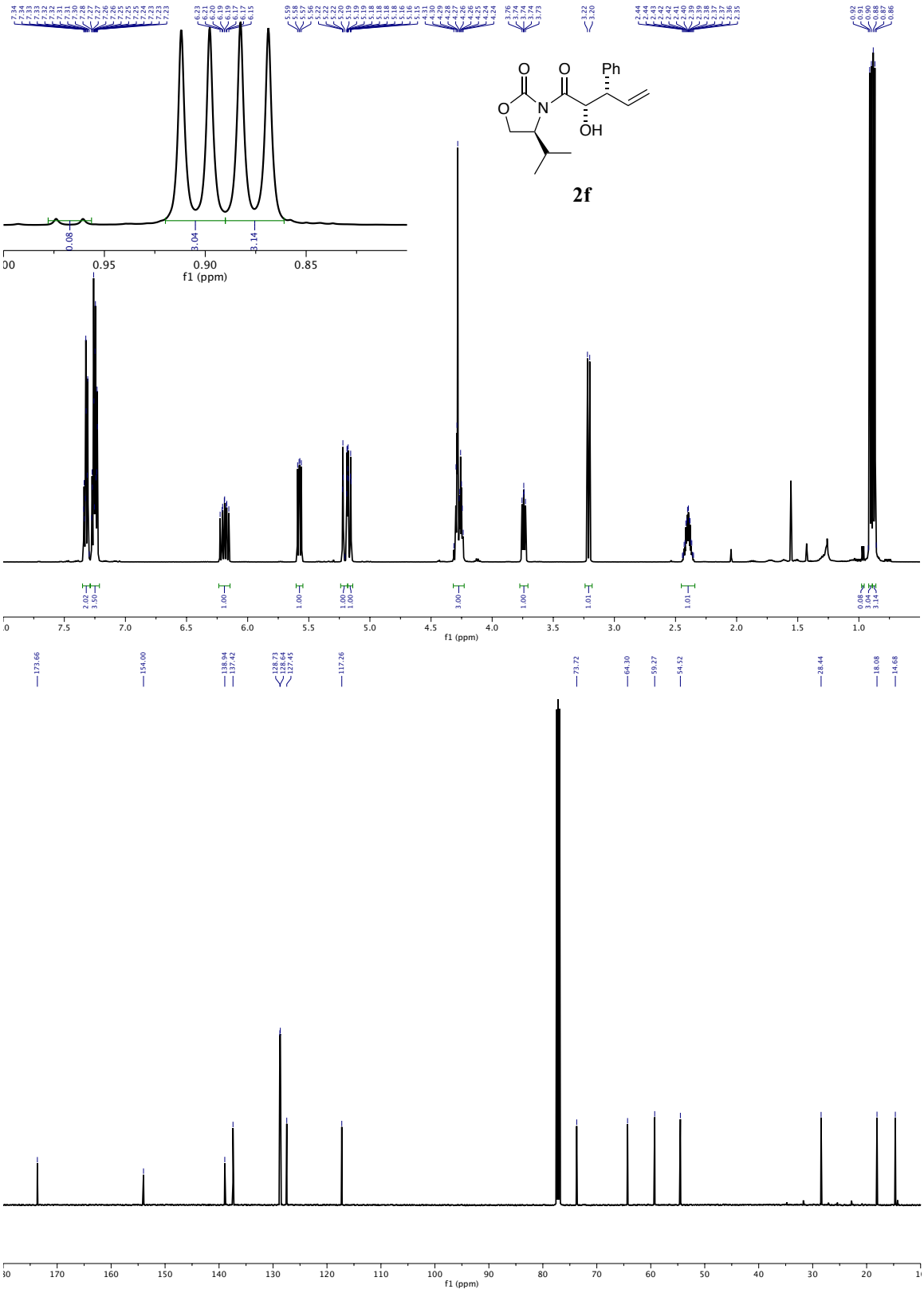


Figure A.3.40. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2f** in $CDCl_3$.

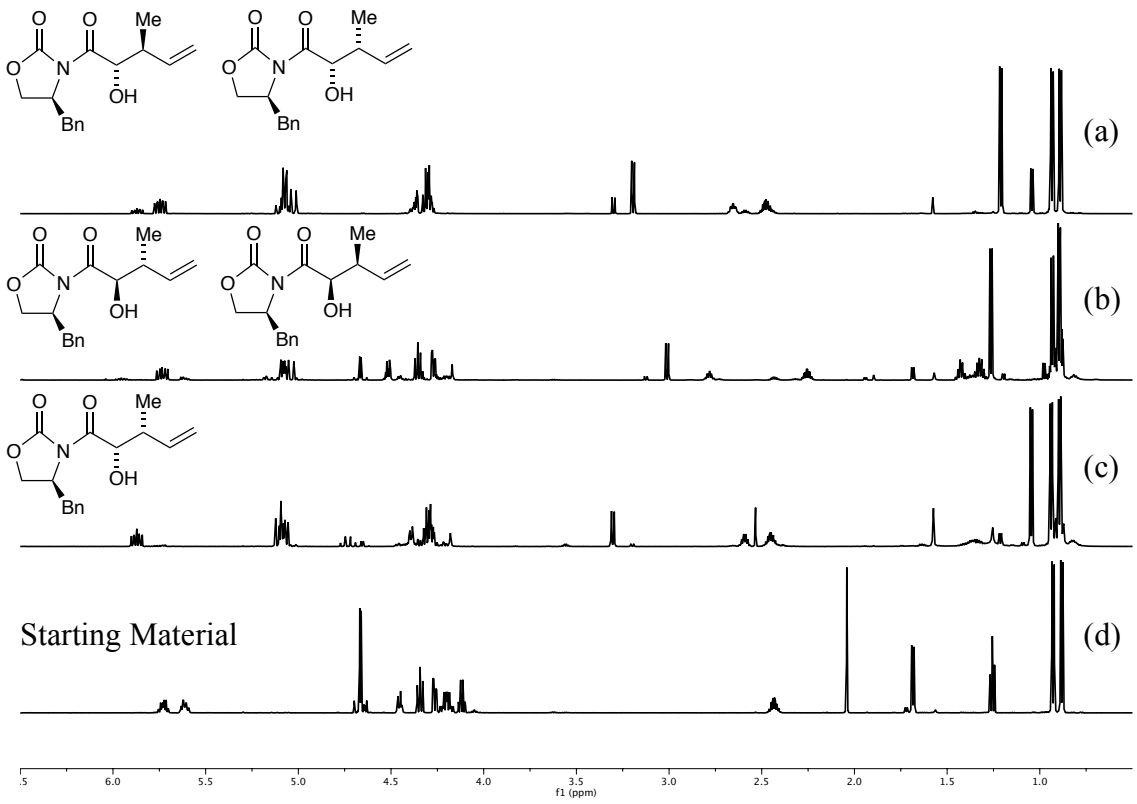


Figure A.3.41. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) **1g** rearrangement major product; (b) **1g** minor product; (c) **2d**; (d) **1g**.

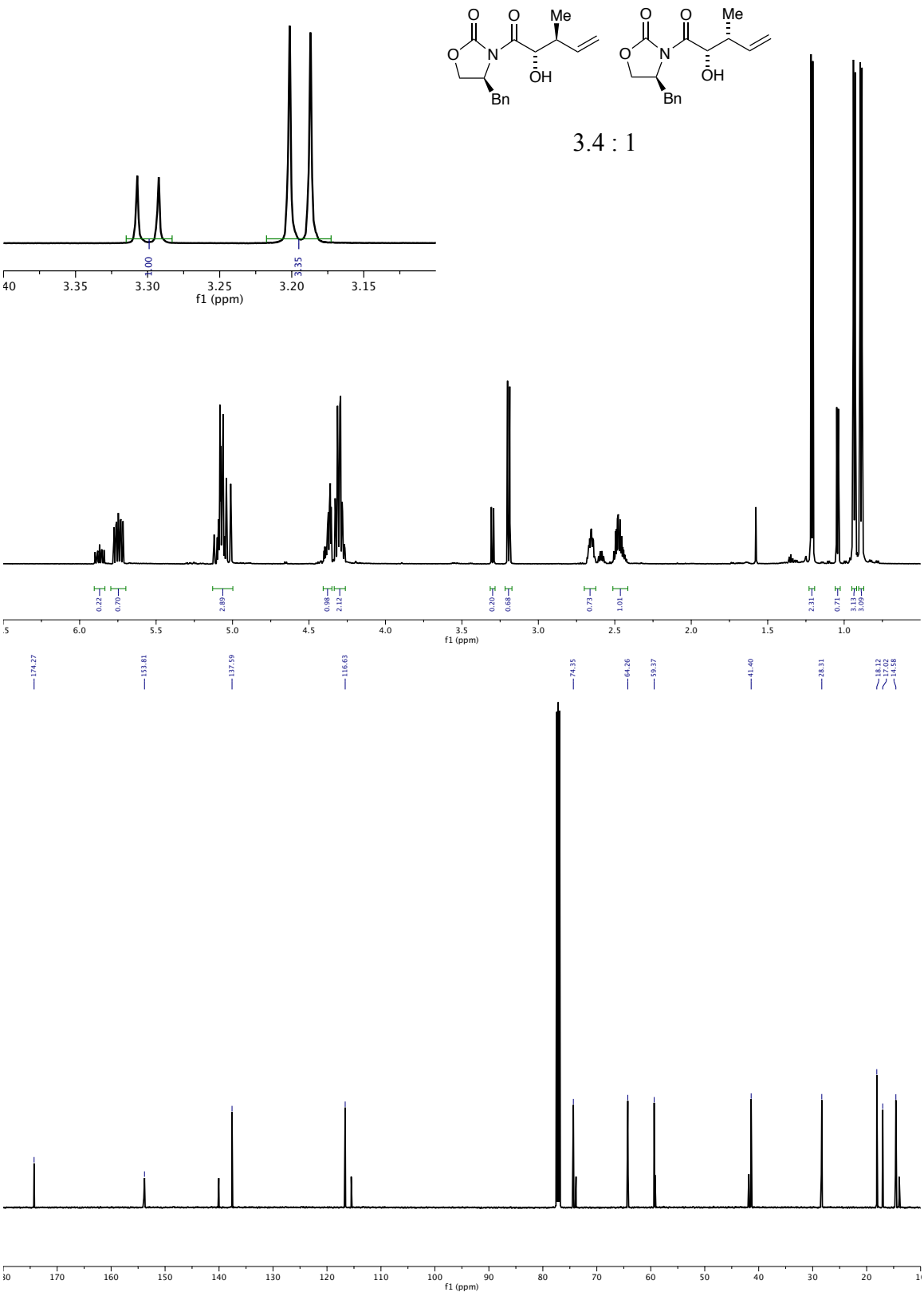


Figure A.3.42. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1g** major product in $CDCl_3$.

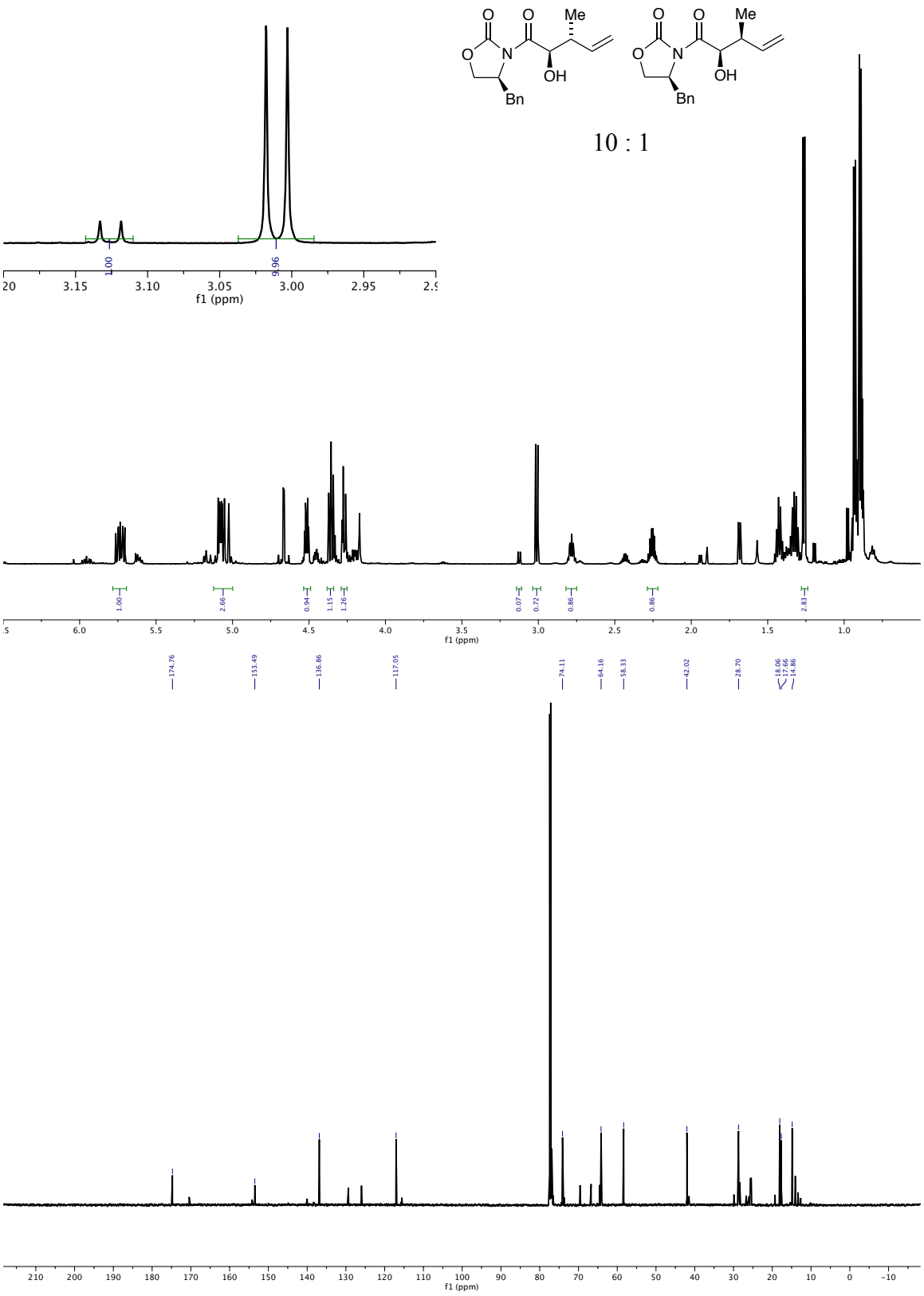
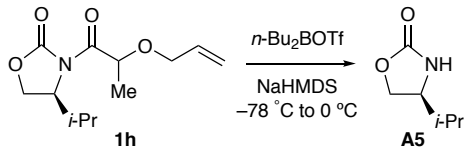


Figure A.3.43. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1g** minor product in $CDCl_3$.



Rearrangement of 1h. Following the procedure for **1d** except using **1h** showed no reactivity even with heating to 60 ºC. Using NaHMDS in place of Et_3N afforded the deacylated product.

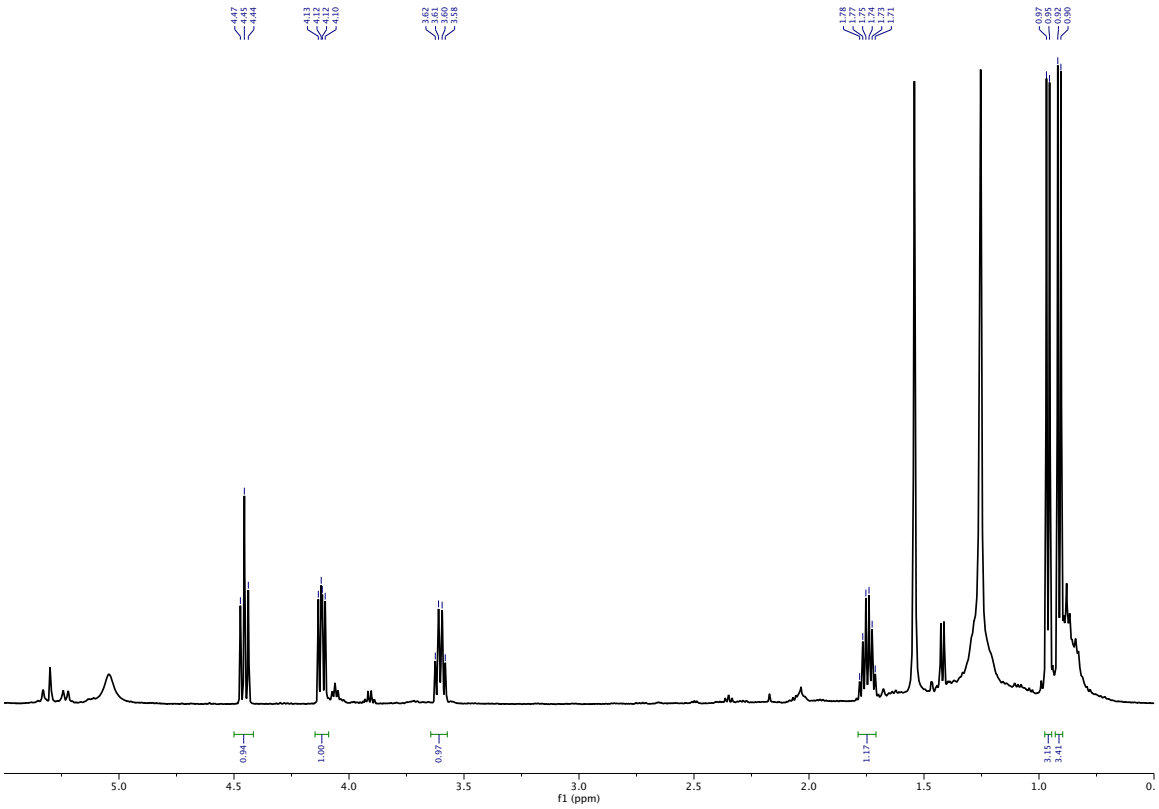
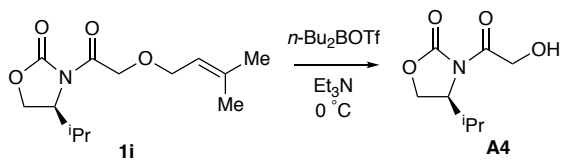


Figure A.3.44. ^1H NMR spectrum of **1h** decomposition product in $CDCl_3$.



Decomposition of 1i. Following the procedure for **1d** except using **1i** afforded a decomposition product.

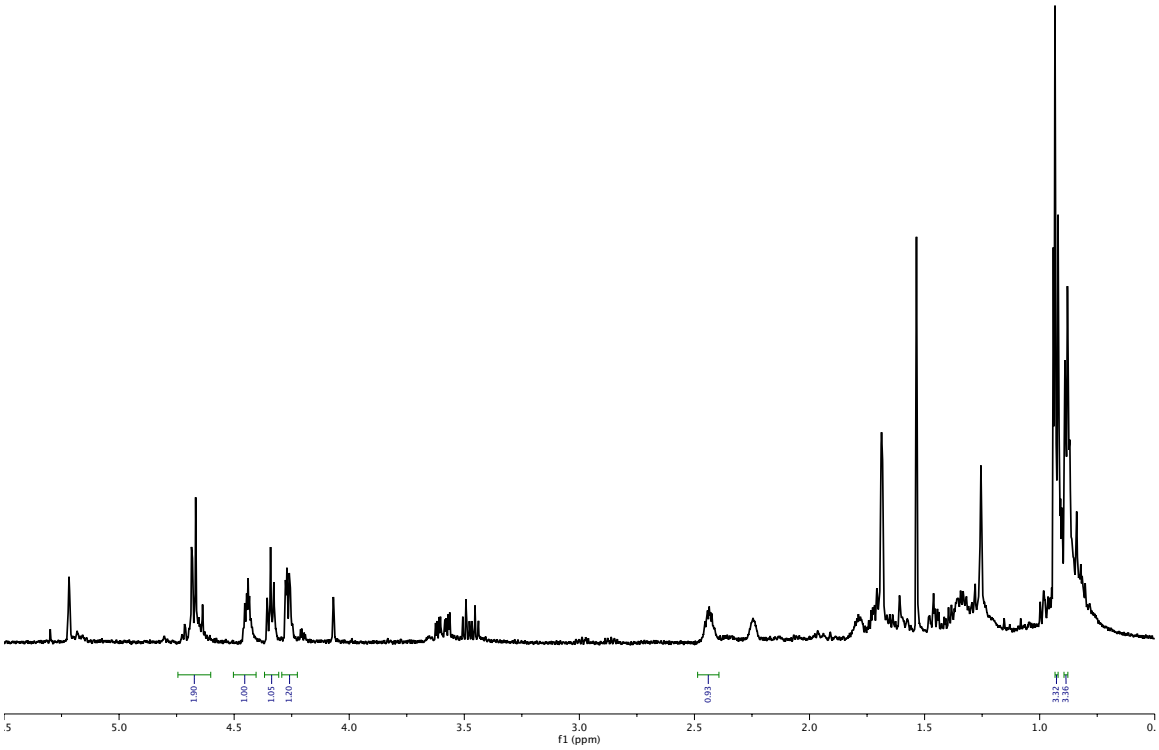
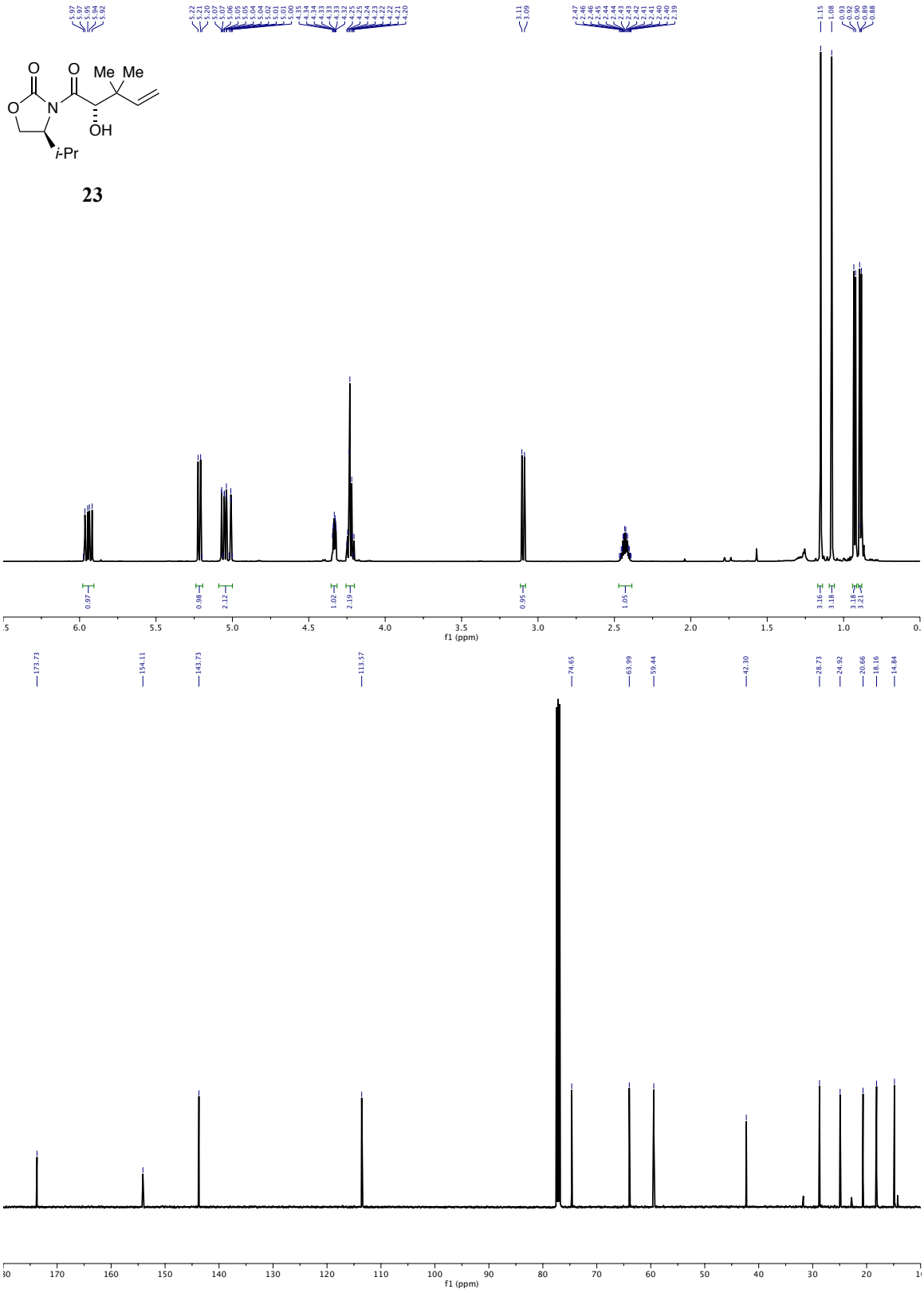


Figure A.3.45. ^{1}H NMR spectrum of **1i** decomposition product in $CDCl_3$.



23

Figure A.3.46. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **23** in $CDCl_3$.

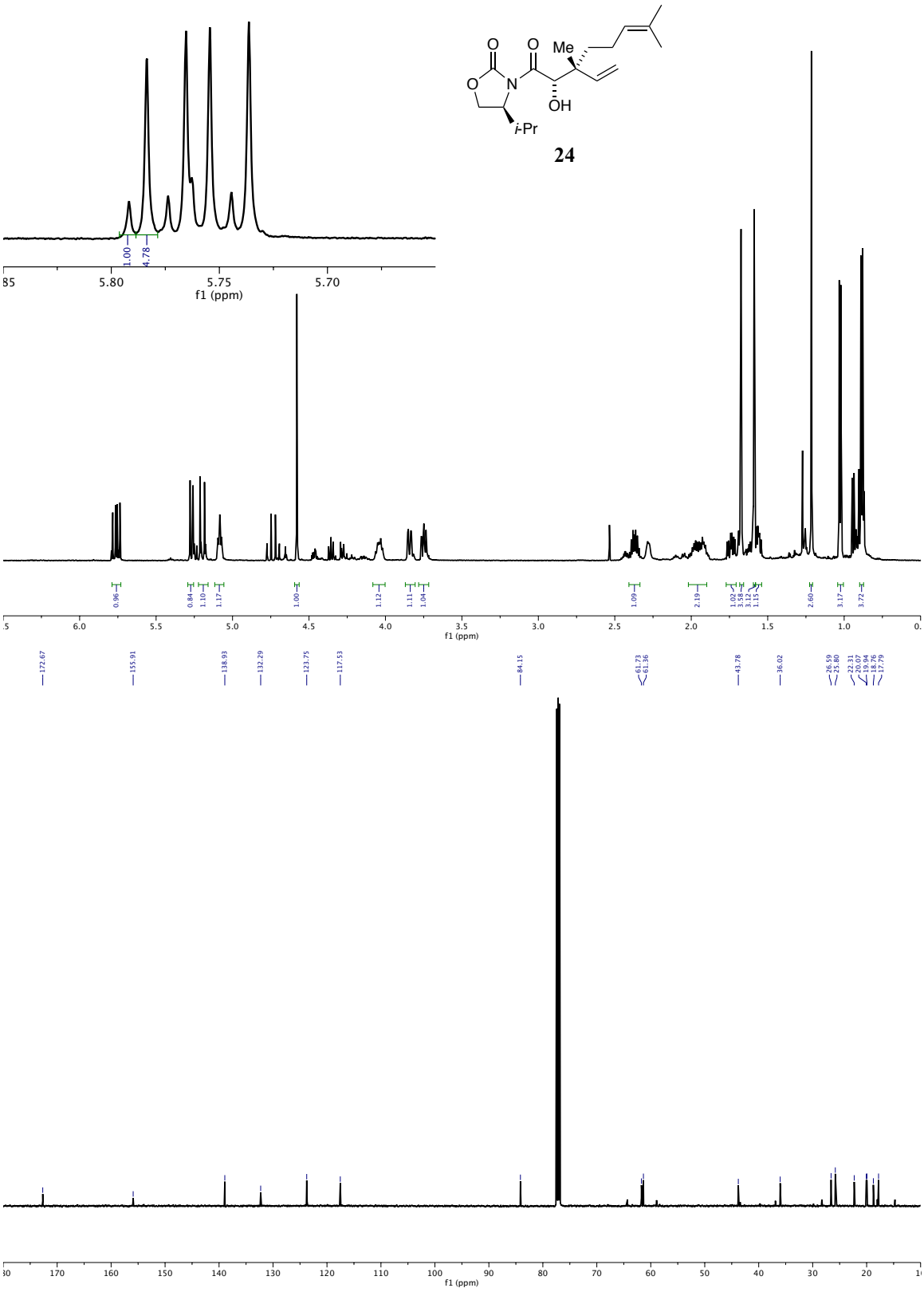


Figure A.3.47. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **24** major in $CDCl_3$.

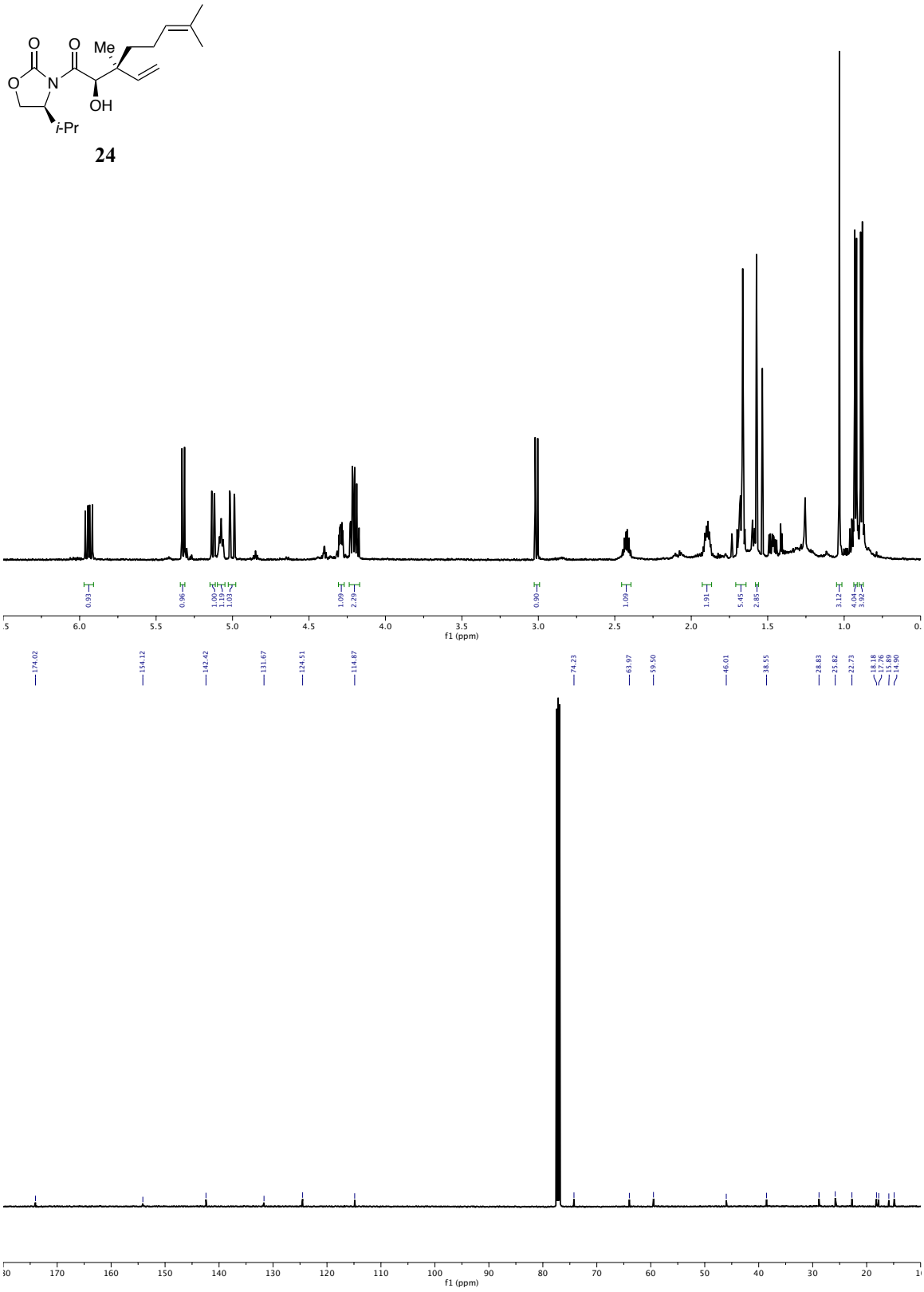
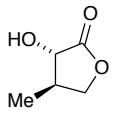


Figure A.3.48. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **24** minor in $CDCl_3$.

6. Products characterization



6

Figure A.3.49. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **6** in $CDCl_3$.

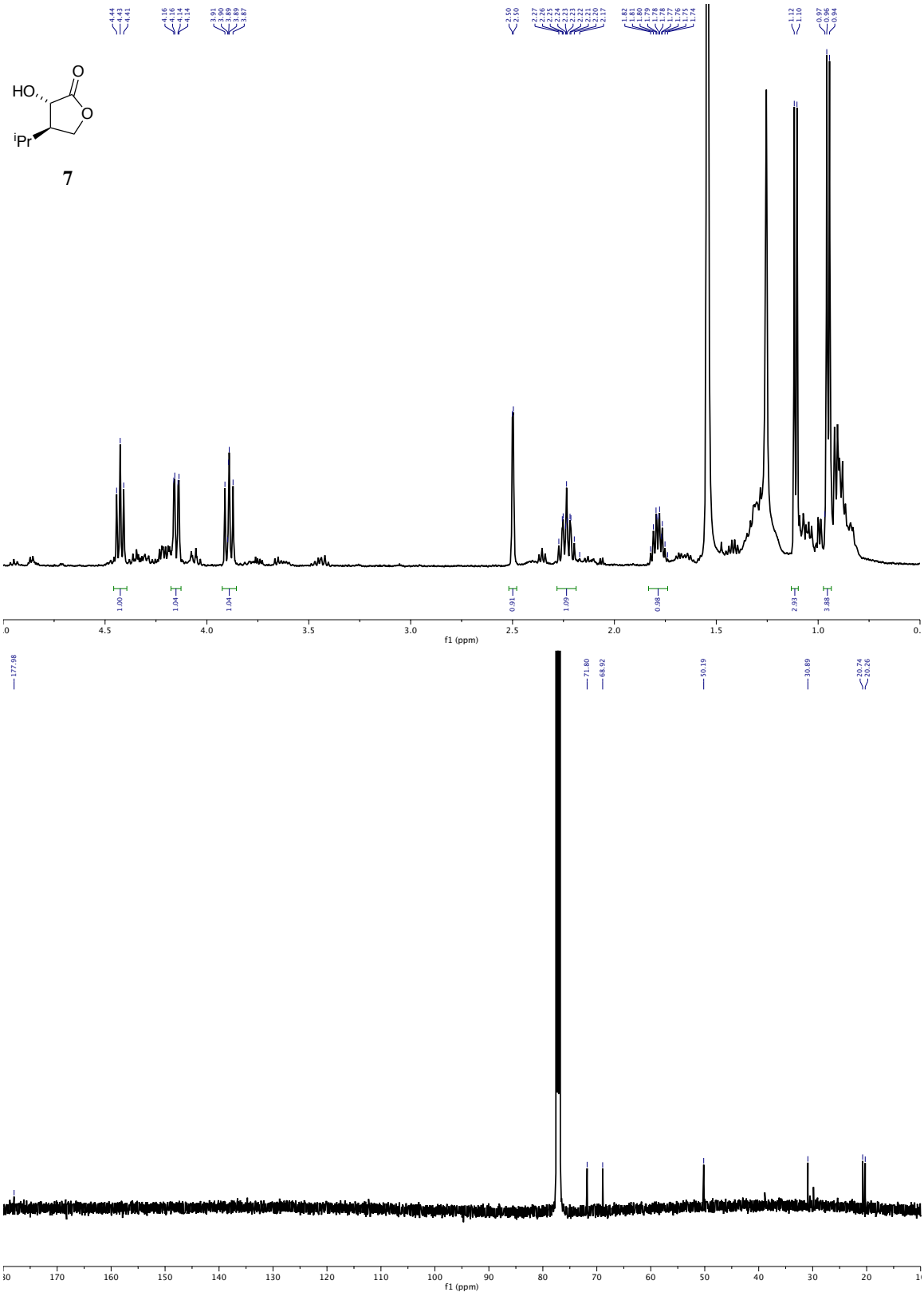


Figure A.3.50. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **7** in $CDCl_3$.

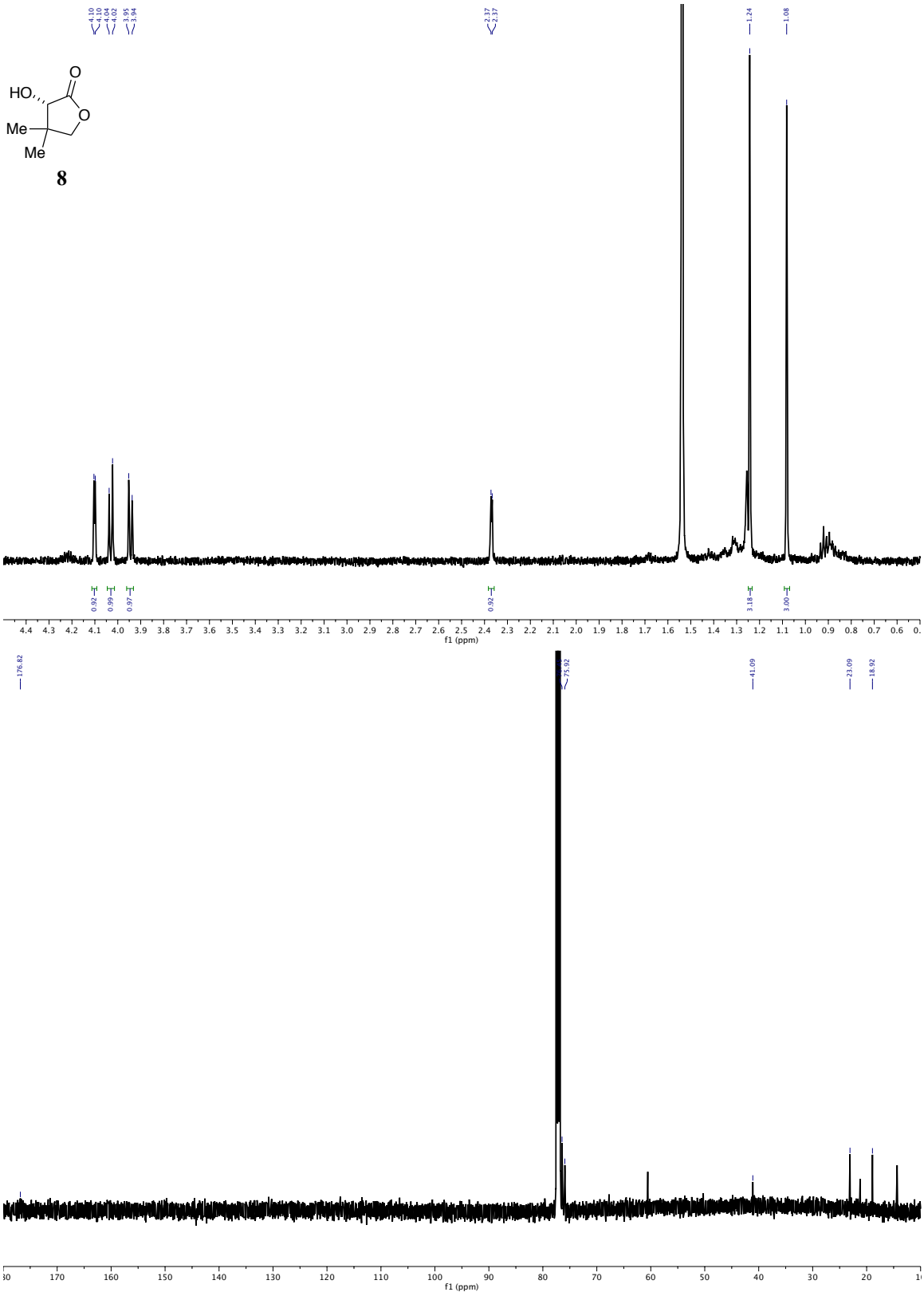


Figure A.3.51. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **8** in $CDCl_3$.

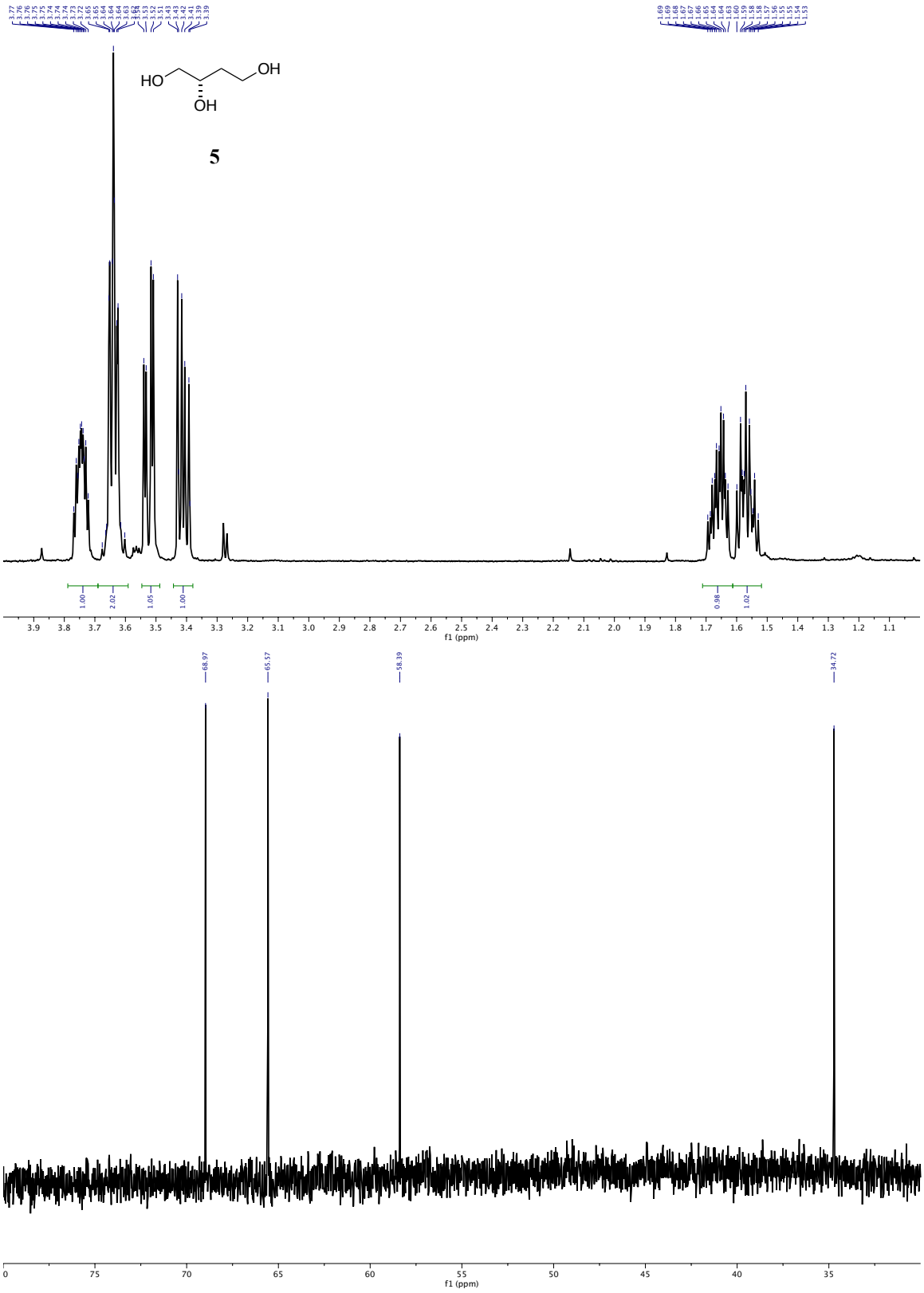


Figure A.3.52. ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra of **5** in D_2O.

7. Using sodium and lithium

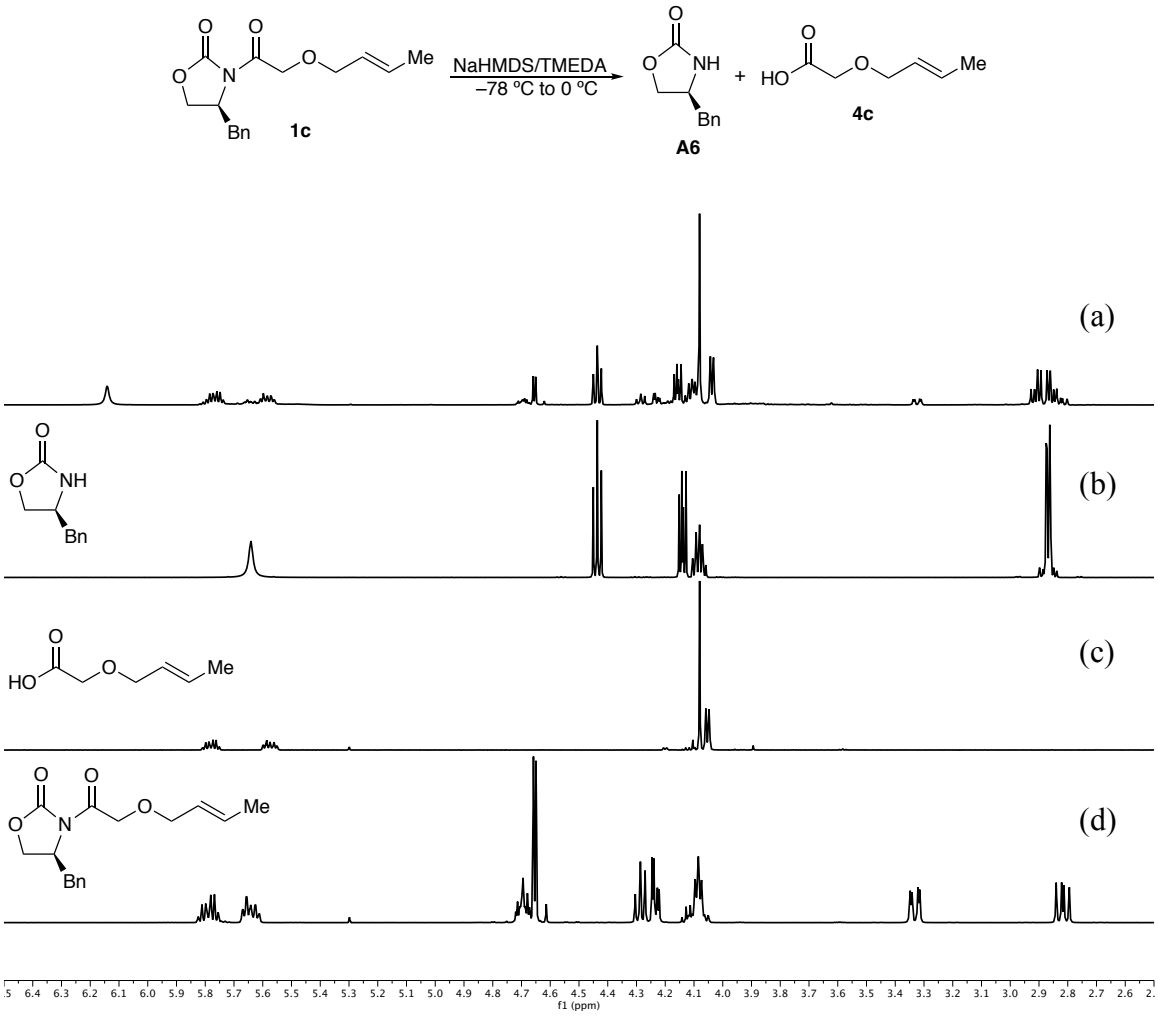


Figure A.3.53. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) products of **1c** reacting with NaHMDS; (b) (*S*)-4-benzyl-2-oxazolidinone; (c) **4c**; (d) **1c**. Using NaHMDS resulted in deacylation prior to rearrangement.

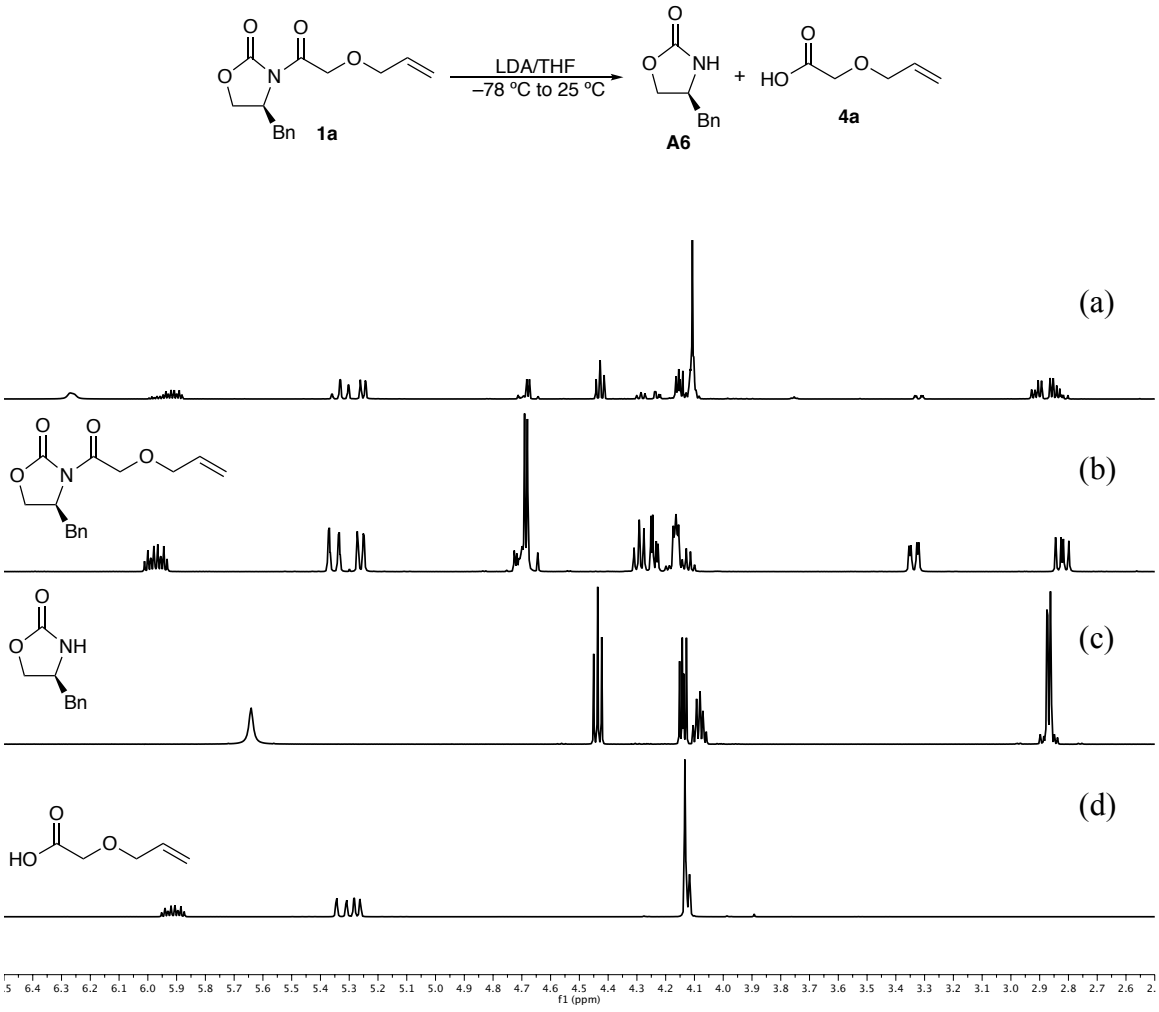
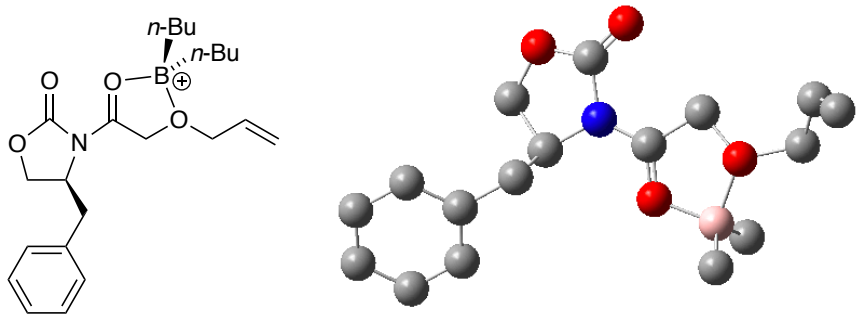


Figure A.3.54. ^{1}H NMR spectra in $CDCl_3$ recorded at 25 ºC of (a) products of **1a** reacting with NaHMDS; (b) **1a**; (c) (*S*)-4-benzyl-2-oxazolidinone; (d) **4a**. Using LDA resulted in deacylation prior to rearrangement.

8. Computation

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 273 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table A.3.3. Geometric coordinates and thermally corrected MP2 energies for boron complex **13** (5 member ring chelation).



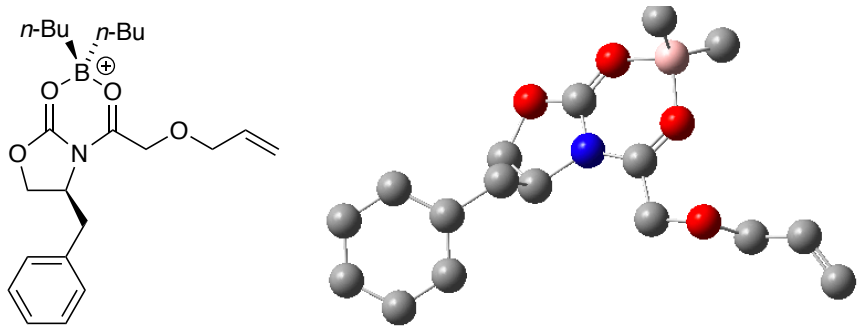
G = –1041.643803 Hartree

G_{MP2} = –651581.3129 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.96758800	0.17667100	0.46728000
H	-0.08745200	0.09270400	-1.08511500	C	0.64542400	-1.33013900	0.44145200
H	0.59396200	-2.08155100	-0.34896800	C	0.08494500	-1.90151600	1.76354100
H	0.71614500	-2.74409800	2.06743600	H	0.16436500	-1.13401600	2.54285100
C	-1.35482900	-2.34740100	1.60542600	C	-1.65754100	-3.53126500	0.91707400
C	-2.98158200	-3.93320700	0.74557800	C	-4.02164800	-3.15638600	1.26188200
C	-3.73135700	-1.98014300	1.95363200	C	-2.40486700	-1.57809000	2.12358000
H	-2.18612300	-0.67002400	2.68189900	H	-4.53437300	-1.37782900	2.36815700
H	-5.05259800	-3.47183700	1.13210700	H	-3.20150300	-4.85595900	0.21662000
H	-0.85353600	-4.15231400	0.52608500	N	2.05249000	-0.87747400	0.58735300
C	3.11697100	-1.66861900	0.66414600	O	3.00121500	-2.92336400	0.54964600
B	4.34245600	-3.73510000	0.53680100	C	4.72733000	-4.10375500	-0.95745500
H	5.71201700	-4.58227300	-1.02224200	H	4.00997300	-4.83527800	-1.35078600
H	4.72528900	-3.25299800	-1.65254800	C	4.36233300	-4.80503300	1.69931900
H	3.65875900	-5.61735900	1.47654000	H	5.34743900	-5.27800300	1.79878500
H	4.09165100	-4.39281900	2.67860700	O	5.24446800	-2.39896600	1.05171400
C	6.72366100	-2.34927800	0.86437600	H	7.02936700	-3.38016000	1.03956900
H	6.89296500	-2.08565600	-0.18485300	C	7.36844700	-1.39938400	1.81950500
H	7.30549500	-0.33753500	1.58708800	C	8.04930500	-1.81101600	2.89116300

H	8.15378700	-2.86542600	3.13709900	H	8.54110200	-1.10684800	3.55557100
C	4.52882000	-1.16859900	0.87222200	H	4.62248200	-0.53423900	1.75482200
H	4.88467800	-0.61136600	-0.00327900	C	2.12461000	0.56209300	0.68338700
O	0.90901300	1.04047400	0.45633900	O	3.12390900	1.18054300	0.92566000

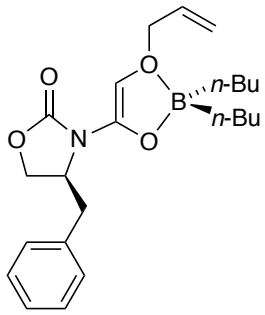
Table A.3.4. Geometric coordinates and thermally corrected MP2 energies for boron complex **12** (6 member ring chelation).

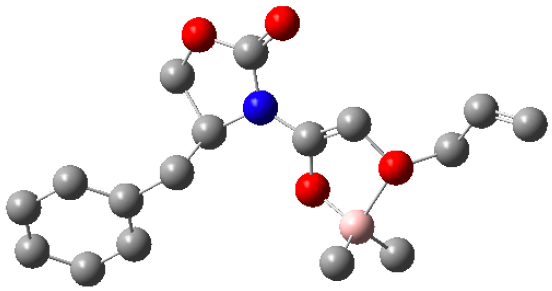


G = –1041.631708 Hartree
G_{MP2} = –651569.4126 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.01385600	-0.26887800	0.29022900
H	-0.06364400	0.13859100	-1.08090800	C	-0.57399600	1.18075300	0.81273600
H	-0.61168300	2.08581100	0.20300200	C	0.17172000	1.44054300	2.14044600
H	-0.38913800	2.18000800	2.72451800	H	0.18073800	0.51402700	2.72715600
C	1.58691700	1.92387500	1.89161700	C	1.82207600	3.23285900	1.44665500
C	3.12093100	3.67278700	1.19471600	C	4.20179900	2.80843600	1.38579700
C	3.97918200	1.50608800	1.83400100	C	2.67789800	1.06607800	2.08503500
H	2.51463200	0.05668100	2.45746800	H	4.81626400	0.83405200	1.99772600
H	5.21359600	3.15298400	1.19473400	H	3.29042000	4.69153300	0.85900600
H	0.98951900	3.92204100	1.31471000	N	-1.96111500	0.66896900	1.03345400
C	-3.10737900	1.33797800	1.38148300	O	-4.14576400	0.70243700	1.64350500
B	-4.32936100	-0.89576900	1.78812800	O	-2.96090100	-1.43652900	1.05731800
C	-1.99196100	-0.70506200	0.82733100	O	-0.86702900	-1.13945400	0.33119600
C	-4.22380200	-1.25248500	3.32526100	H	-3.31272900	-0.88095800	3.81370100
H	-5.07845300	-0.84153000	3.87571100	H	-4.24876600	-2.33991000	3.46493100
C	-5.54400500	-1.33003200	0.88099300	H	-6.48473300	-0.93184700	1.27976900
H	-5.45938500	-0.99782200	-0.16126400	H	-5.64128900	-2.42211600	0.86928300
C	-3.10637500	2.86270800	1.41522500	O	-4.29491000	3.38876500	1.87687300
C	-5.31777900	3.58398600	0.86503800	H	-4.94084500	4.28160800	0.10403800
H	-5.53103400	2.61921600	0.38259600	C	-6.53942400	4.12520300	1.53535700
H	-6.96671100	3.49971900	2.31687900	C	-7.10876400	5.28229500	1.20068600
H	-6.69680800	5.92302500	0.42393800	H	-8.01589000	5.63067700	1.68518100
H	-2.82827200	3.21721700	0.40539500	H	-2.30402700	3.17884400	2.09608000

Table A.3.5. Geometric coordinates and thermally corrected MP2 energies for enolate **15** (5 member ring chelation).

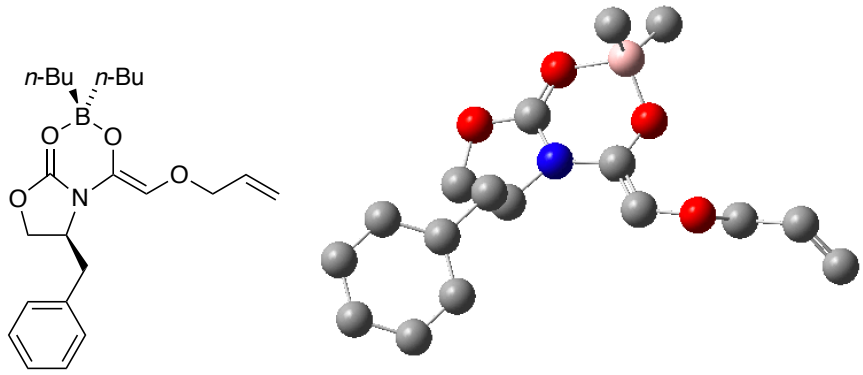




G = –1041.249187 Hartree
G_{MP2} = –651337.4921 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.01422700	0.14153800	0.37614500
H	0.01076000	0.15153700	-1.08498600	C	0.61152500	-1.35589600	0.39922300
H	0.58082000	-2.06584500	-0.42968800	C	-0.03226900	-1.99403200	1.65247100
H	0.61764000	-2.81329900	1.97746900	H	-0.04686000	-1.24883700	2.45723500
C	-1.42945700	-2.51017100	1.38324900	C	-1.61867400	-3.68522100	0.63990700
C	-2.90122000	-4.15383200	0.35735400	C	-4.02060300	-3.45524400	0.81643000
C	-3.84680600	-2.28871200	1.56131800	C	-2.56057600	-1.82143500	1.84071700
H	-2.43311000	-0.91730200	2.43248500	H	-4.71099500	-1.74239200	1.92996300
H	-5.02024700	-3.82176000	0.59934500	H	-3.02740200	-5.06822300	-0.21644800
H	-0.75119600	-4.24057000	0.28914700	N	1.99268400	-0.92523800	0.63789800
C	3.06064700	-1.80824200	0.79610400	C	4.29341300	-1.53681900	1.26129700
H	4.69857600	-0.62536600	1.66189700	O	5.09554300	-2.71063200	1.25393800
C	6.29645000	-2.62021200	0.41757500	H	6.66930700	-3.64291200	0.34861700
H	5.98579300	-2.27674200	-0.57619600	C	7.32309100	-1.71222900	1.02277200
H	7.06729900	-0.65586600	1.08642800	C	8.51680000	-2.13491300	1.43925500
H	8.80513900	-3.18252700	1.38200600	H	9.25478200	-1.45021700	1.84781000
B	3.82491500	-4.01291900	0.92018400	O	2.80549400	-3.06635900	0.41090500
C	4.37306600	-4.99770300	-0.20455600	H	5.22393800	-5.60620200	0.12640800
H	3.57031100	-5.70632300	-0.45437500	H	4.64677600	-4.49754900	-1.14191200
C	3.55324900	-4.55869800	2.39258200	H	2.73733700	-5.29580700	2.37145200
H	4.42918400	-5.06908000	2.81195500	H	3.26056000	-3.77059400	3.09763500
C	2.07462000	0.44091500	0.86189300	O	0.85251600	0.99028900	0.60843100
O	3.03669400	1.07415100	1.22546000				

Table A.3.6. Geometric coordinates and thermally corrected MP2 energies for enolate **14** (6 member ring chelation).

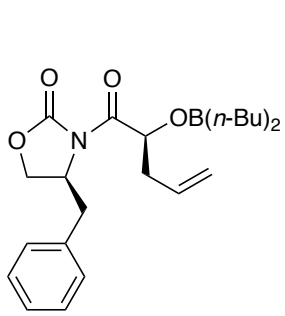


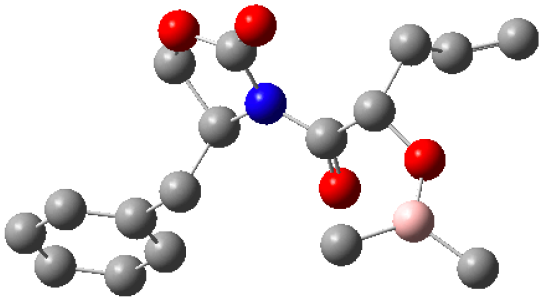
G = –1041.252377 Hartree

G_{MP2} = –651335.8477 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.01796900	-0.26678000	0.28286400
H	-0.05694100	0.15631700	-1.08116400	C	-0.56958200	1.18900500	0.80032400
H	-0.58493500	2.09721700	0.19138100	C	0.15791800	1.45437200	2.13969500
H	-0.45121700	2.15287100	2.72302000	H	0.19195900	0.51547300	2.70533300
C	1.55528200	2.00064000	1.93889100	C	1.74984000	3.33357000	1.54670700
C	3.03289800	3.83599300	1.33275700	C	4.14698600	3.01207200	1.50945200
C	3.96834100	1.68616300	1.90447700	C	2.68173200	1.18623400	2.11651800
H	2.55191200	0.15553800	2.44013100	H	4.82916200	1.04010300	2.05403800
H	5.14711100	3.40398300	1.34663200	H	3.16346200	4.87282300	1.03485800
H	0.88979100	3.98848600	1.42071500	N	-1.94341400	0.70942600	1.00049200
C	-3.09585900	1.46651200	1.39360400	C	-3.01240900	2.80145600	1.56072700
H	-2.07280700	3.33237300	1.43644900	O	-4.06330200	3.59480600	1.94105000
C	-5.19266900	3.63268500	1.04362800	H	-4.87710700	4.01290600	0.06138000
H	-5.57968000	2.61528500	0.91163800	C	-6.23358700	4.51949700	1.65441700
H	-6.51064500	4.27193500	2.67855700	C	-6.83078400	5.52684400	1.01894500
H	-6.56653400	5.79700700	-0.00169100	H	-7.61345000	6.11638100	1.48869300
O	-4.21539600	0.75290700	1.44239900	B	-4.23560200	-0.65830600	1.93617100
O	-2.97786200	-1.36731500	1.06474000	C	-2.01032000	-0.62319900	0.81649100
O	-0.86385200	-1.11902400	0.33398100	C	-3.79726900	-0.81426100	3.47346300
H	-2.84818100	-0.31658800	3.72299500	H	-4.56130700	-0.37015000	4.12557600
H	-3.69869300	-1.86721300	3.76655200	C	-5.55992300	-1.39208300	1.43602000
H	-6.44156300	-0.98621000	1.95012000	H	-5.72672300	-1.26697400	0.35830000
H	-5.53370400	-2.46857600	1.64699400				

Table A.3.7. Geometric coordinates and thermally corrected MP2 energies for rearrangement product **17** (no chelation).

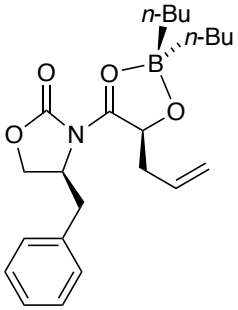


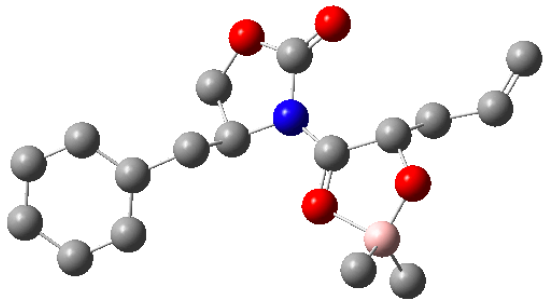


G = –1041.307135 Hartree
G_{MP2} = –651375.0352 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.02873900	0.02587400	-0.36052800
H	-0.09401800	0.63400200	0.88800600	C	-0.52814700	-1.42193700	0.23514100
H	-0.51373600	-1.69522300	1.29178500	C	0.20238700	-2.50478600	-0.59216400
H	-0.39301400	-3.42041400	-0.53282600	H	0.22407600	-2.19053200	-1.64300800
C	1.60697000	-2.75988400	-0.08857300	C	1.81008600	-3.47563200	1.10116200
C	3.09694700	-3.69541400	1.59099700	C	4.20552900	-3.20364500	0.89725200
C	4.01748500	-2.49473900	-0.28927100	C	2.72695300	-2.27506200	-0.77640000
H	2.58903900	-1.73343400	-1.71001400	H	4.87387500	-2.11543100	-0.84044400
H	5.20863200	-3.37775000	1.27686900	H	3.23527200	-4.25630600	2.51151700
H	0.95125000	-3.87162000	1.63928000	N	-1.92425100	-1.23930900	-0.19872500
C	-2.89986000	-2.19156200	0.13326200	C	-4.35287300	-1.93356500	-0.30024700
H	-4.35296900	-1.61576100	-1.34617600	C	-5.00778100	-0.81236000	0.54234900
H	-4.47007200	0.12114300	0.33686000	H	-6.02543300	-0.68208600	0.15822700
C	-5.04967100	-1.09111300	2.02057600	H	-4.09178700	-1.27383200	2.50944000
C	-6.16245400	-1.11462700	2.75291100	H	-7.14193900	-0.94879300	2.30905500
H	-6.13911200	-1.30284400	3.82286600	O	-5.11402400	-3.10969700	-0.11883400
B	-4.95608900	-4.26536300	-0.83712400	C	-5.90003900	-5.46054300	-0.41475300
H	-6.61472200	-5.68762300	-1.21951000	H	-5.32419500	-6.38341100	-0.26052500
H	-6.46973500	-5.25068700	0.49606200	C	-3.91714000	-4.41913600	-2.02630800
H	-4.30609000	-5.07611100	-2.81340000	H	-3.59760800	-3.48229400	-2.49886800
H	-3.01071900	-4.90810900	-1.64002300	O	-2.56964700	-3.16888100	0.78096700
C	-2.03241300	-0.13076000	-1.05631100	O	-0.85371200	0.53822800	-1.03394500
O	-2.97711000	0.20778200	-1.72478600				

Table A.3.8. Geometric coordinates and thermally corrected MP2 energies for rearrangement product **16** (chelated).

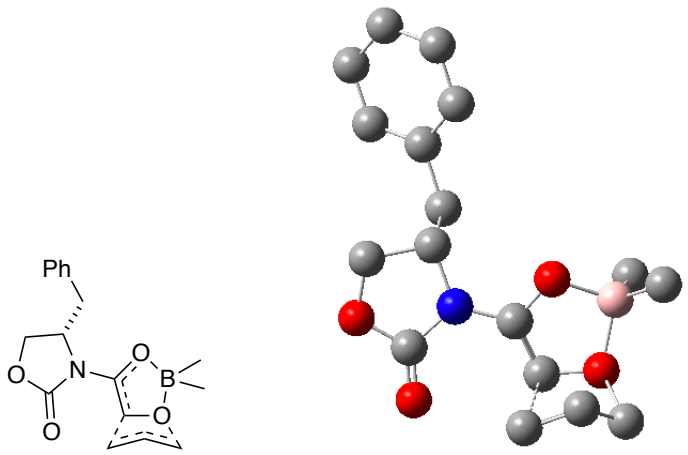




G = –1041.296955 Hartree
G_{MP2} = –651370.1006 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.01034800	0.29279500	0.28541500
H	0.14731600	0.17908000	-1.06966000	C	0.35434200	-1.43808300	0.41025100
H	0.29894400	-2.12683900	-0.43473100	C	-0.48274300	-1.98294700	1.58947000
H	-0.00330700	-2.90027000	1.94487600	H	-0.45143400	-1.25577900	2.40999700
C	-1.91498300	-2.26255100	1.18487900	C	-2.22108800	-3.38970700	0.40754500
C	-3.53178500	-3.64363700	0.00539700	C	-4.56042200	-2.77410500	0.37625800
C	-4.26986500	-1.65335400	1.15427700	C	-2.95573500	-1.40062700	1.55436200
H	-2.73986500	-0.53291900	2.17453400	H	-5.06486200	-0.97679100	1.45598100
H	-5.58231700	-2.97381800	0.06605200	H	-3.75140700	-4.52446900	-0.59179800
H	-1.42762200	-4.07950500	0.12713300	N	1.77020900	-1.23925700	0.78052400
C	2.64262500	-2.27265400	0.93157300	C	4.12547800	-2.16040800	1.28424700
H	4.24631600	-1.52415700	2.17052300	O	4.49350000	-3.47132700	1.56613300
B	3.61264600	-4.50872100	1.01770200	O	2.23313900	-3.43672400	0.74457700
C	3.12404600	-5.56588100	2.11529300	H	2.32972200	-6.22847300	1.74729800
H	3.96513300	-6.21279700	2.40264600	H	2.76879600	-5.08528800	3.03657400
C	3.95389900	-5.06625000	-0.45093200	H	4.85377200	-5.69555200	-0.40007500
H	3.15149700	-5.69984300	-0.85190000	H	4.16021400	-4.28656500	-1.19740400
C	4.94581500	-1.52039400	0.12441600	H	4.60879800	-0.49299100	-0.04501400
H	4.75788600	-2.10294800	-0.78715100	C	6.41495800	-1.53721100	0.44540400
H	6.83476700	-2.51909300	0.65508900	C	7.18859300	-0.45259300	0.49600500
H	6.79564800	0.54372100	0.30252400	H	8.24722800	-0.51903900	0.73295500
C	2.02340900	0.12435600	1.08388400	O	0.93101800	0.83253700	0.72947200
O	3.01256000	0.58993900	1.57987200				

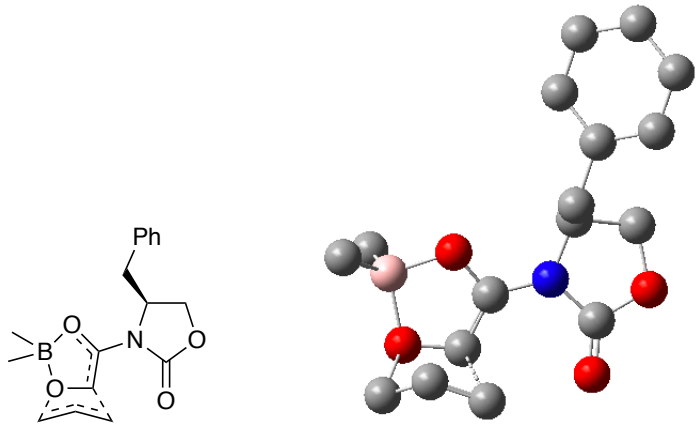
Table A.3.9. Geometric coordinates and thermally corrected MP2 energies for transition structure **18$_A$**.



G = –1041.231479 Hartree
G_{MP2} = –651325.2492 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.03561400	0.16126400	0.30201500
H	0.10540400	0.21886900	-1.06792100	C	0.52449600	-1.40432800	0.35928900
H	0.57376700	-2.04799500	-0.52137900	N	1.88191200	-1.04918800	0.78931300
C	2.89768900	-1.97320900	0.95660400	C	4.10591700	-1.81955400	1.60147500
H	4.47701500	-0.96214500	2.13727900	O	4.82468800	-2.96179200	1.53749400
B	3.75472400	-4.10882700	1.10969300	O	2.68115200	-3.18224400	0.48908500
C	4.31967900	-5.15090400	0.03444500	H	4.62023700	-4.70458400	-0.92127900
H	5.17493600	-5.71702100	0.42759100	H	3.54358000	-5.89346200	-0.19563200
C	3.21394400	-4.74307400	2.48905900	H	4.00702700	-5.29442000	3.01102800
H	2.82794400	-3.99140000	3.19066300	H	2.40448800	-5.45978800	2.29365300
C	6.36106100	-2.71651100	0.30410200	C	5.77136500	-2.02152200	-0.77311100
H	5.42893300	-2.59513800	-1.63129800	C	5.36810300	-0.72697300	-0.62988000
H	4.77216100	-0.22748300	-1.38830100	H	5.71305700	-0.10623500	0.19009700
H	6.89537600	-2.15896500	1.06656700	H	6.65122800	-3.75500400	0.20152700
C	2.00066000	0.30771000	1.07660200	O	0.83461900	0.91856300	0.73560600
O	2.95355100	0.87780400	1.54916300	C	-0.27335100	-2.11561700	1.47612200
H	-0.34953800	-1.44108300	2.33767600	H	0.30852700	-2.98764400	1.79274600
C	-1.65035500	-2.54222500	1.01458800	C	-2.79886200	-1.84723900	1.41550600
C	-4.06325500	-2.23020900	0.96237500	C	-4.19645500	-3.31656300	0.09754200
C	-3.05940500	-4.02033600	-0.30708300	C	-1.79874700	-3.63614900	0.14849200
H	-0.91871000	-4.19649900	-0.16052200	H	-3.15527700	-4.87349200	-0.97345800
H	-5.17928300	-3.61770200	-0.25463500	H	-4.94249300	-1.68160100	1.28960600
H	-2.70406200	-1.00678400	2.09999200				

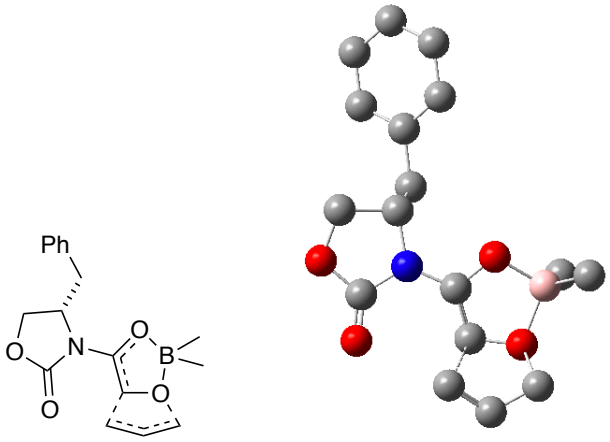
Table A.3.10. Geometric coordinates and thermally corrected MP2 energies for transition structure **18$_B$**.



G = –1041.23127 Hartree
G_{MP2} = –651324.9035 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.98670200	0.16551600	-0.43400200
H	0.06570100	0.05835700	1.09168900	C	-0.66065800	-1.30737400	-0.47296200
H	-0.58201600	-2.09482000	0.27985000	N	-2.05082800	-0.84449600	-0.56244700
C	-2.12367900	0.54307100	-0.66636700	O	-0.87847400	1.04944100	-0.45967200
O	-3.09954800	1.21241700	-0.90193300	C	-3.13513900	-1.69276200	-0.69950100
C	-4.47687000	-1.37874800	-0.70223300	H	-4.94282500	-0.41423700	-0.58960200
O	-5.22443700	-2.49795600	-0.82437900	B	-4.21196200	-3.72018900	-0.47493300
O	-2.87959800	-2.98124200	-0.75505000	C	-4.37499600	-3.99200500	1.10470900
H	-5.37162800	-4.38907600	1.33823200	H	-3.64594100	-4.74026600	1.44437300
H	-4.23292800	-3.09220700	1.71779100	C	-4.38492100	-4.99446500	-1.42746900
H	-5.38411300	-5.44085700	-1.33269800	H	-4.20229700	-4.79825500	-2.49106000
H	-3.67382500	-5.77494200	-1.12446300	C	-6.04933300	-2.55575700	-2.62572300
H	-6.78985800	-1.82325100	-2.32113200	H	-6.38566100	-3.58537800	-2.61511800
C	-4.98326800	-2.15284700	-3.45851400	C	-4.53467900	-0.86554600	-3.44111000
H	-5.12163400	-0.05952900	-3.01417900	H	-3.62128000	-0.57171200	-3.95018100
H	-4.37731700	-2.92345700	-3.92950000	C	-0.12750400	-1.82738900	-1.82894500
H	-0.16882400	-1.00838600	-2.55787300	H	-0.81248400	-2.60925800	-2.17090900
C	1.28157300	-2.37016400	-1.72542400	C	2.37988600	-1.63716900	-2.19392000
C	3.67907100	-2.13477500	-2.07109600	C	3.89848900	-3.37647400	-1.47441400
C	2.81174900	-4.11899000	-1.00588700	C	1.51580300	-3.61978700	-1.13169900
H	0.67286000	-4.20884500	-0.77621500	H	2.97321000	-5.09107700	-0.54754400
H	4.90813300	-3.76677200	-1.37982600	H	4.51719600	-1.55327200	-2.44594600
H	2.21567500	-0.67380500	-2.67246500				

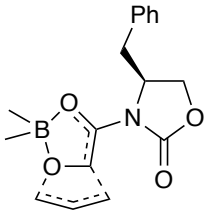
Table A.3.11. Geometric coordinates and thermally corrected MP2 energies for transition structure **18**$_C$.

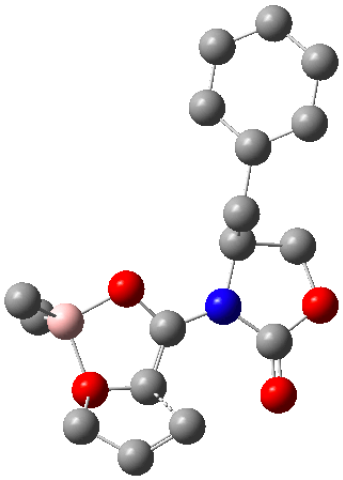


G = –1041.228303 Hartree
G_{MP2} = –651321.3575 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.02474100	0.19097500	0.32124300
H	0.08966700	0.20825700	-1.07152200	C	0.49360900	-1.41521000	0.35937800
H	0.50590100	-2.06688700	-0.51657100	N	1.86943500	-1.09469200	0.75755100
C	2.85998400	-2.04857300	0.91385300	C	4.07754800	-1.92738900	1.54073800
H	4.46016700	-1.09005000	2.09672900	O	4.77376200	-3.08951900	1.45442700
C	6.32629600	-2.91196900	0.24046300	H	7.00300300	-3.53841300	0.81093200
H	5.83015800	-3.39976200	-0.58774100	C	6.51336100	-1.51025400	0.19628200
H	7.22870500	-1.05646800	0.87974300	C	5.61569600	-0.71991600	-0.45301400
H	4.89431000	-1.14523700	-1.14483600	H	5.62579200	0.36182800	-0.36398200
B	3.66295200	-4.20378800	1.02071700	O	2.60712300	-3.24638900	0.42796700
C	4.17397600	-5.24509100	-0.08515900	H	4.34532100	-4.80922400	-1.07853200
H	5.09595500	-5.75669400	0.22161900	H	3.41801500	-6.03045000	-0.21963300
C	3.13660700	-4.84371600	2.40250400	H	3.92341900	-5.43278600	2.89186600
H	2.79834200	-4.09186900	3.12794900	H	2.29656800	-5.52720300	2.21718700
C	2.02944000	0.26029400	1.03579400	O	0.87339200	0.90024300	0.71226800
O	3.00454000	0.80810100	1.48860400	C	-0.29785800	-2.09591300	1.49966000
H	-0.33835100	-1.41185600	2.35606800	H	0.26870100	-2.97954200	1.81209900
C	-1.69453200	-2.49242500	1.07181500	C	-2.81586600	-1.75853600	1.48035900
C	-4.09849500	-2.11429100	1.05729700	C	-4.27763400	-3.21235000	0.21581900
C	-3.16811000	-3.95492300	-0.19576500	C	-1.88909300	-3.59754300	0.22945300
H	-1.03051100	-4.18736600	-0.08492200	H	-3.29975800	-4.81731800	-0.84389500
H	-5.27476100	-3.49245200	-0.11272900	H	-4.95607300	-1.53548700	1.38996500
H	-2.68548000	-0.90894600	2.14752400				

Table A.3.12. Geometric coordinates and thermally corrected MP2 energies for transition structure **18$_D$**.

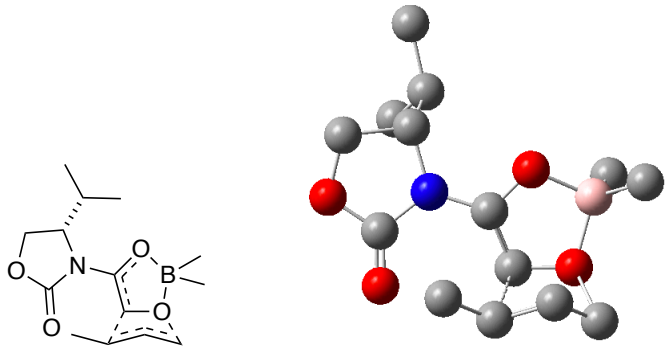




G = –1041.210713 Hartree
G_{MP2} = –651321.2071 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.97677700	0.21524600	-0.43458000
H	0.07520000	0.00993500	1.09263000	C	-0.62515800	-1.30402600	-0.52738300
H	-0.51682900	-2.12216600	0.18810700	N	-2.02975500	-0.88098800	-0.58736400
C	-2.14633800	0.50745700	-0.62213500	O	-0.91433300	1.04163200	-0.40283400
O	-3.14414300	1.15776900	-0.81416500	C	-3.08858900	-1.75794300	-0.74904000
C	-4.43559500	-1.48577900	-0.72656500	H	-4.92384500	-0.54673300	-0.53522200
O	-5.15403800	-2.62504000	-0.90135400	B	-4.08630000	-3.83093600	-0.63639400
O	-2.78693900	-3.03350600	-0.88430500	C	-4.23436300	-4.19936900	0.92437800
H	-5.21264700	-4.65210900	1.13305600	H	-3.47286500	-4.93322000	1.22174800
H	-4.13177000	-3.33016400	1.58719200	C	-4.20879600	-5.05519400	-1.66366200
H	-5.22440400	-5.47150400	-1.69557500	H	-3.90938700	-4.81871400	-2.69354100
H	-3.55375000	-5.87178100	-1.33157700	C	-6.04849400	-2.65195600	-2.65992300
C	-6.05034700	-1.28355000	-3.02185900	C	-4.88662800	-0.66435100	-3.35878400
H	-3.99630500	-1.23974700	-3.59593200	H	-4.81442900	0.41277200	-3.47125300
H	-6.92897500	-0.68310600	-2.79331600	H	-6.96231600	-3.13278200	-2.32882700
H	-5.31635400	-3.30949700	-3.10890800	C	-0.08590000	-1.74544300	-1.90856000
H	-0.15655700	-0.89542500	-2.59874800	H	-0.74943200	-2.53138400	-2.28193100
C	1.33909300	-2.25068400	-1.83708400	C	2.41319600	-1.46527400	-2.27576400
C	3.72697000	-1.92961600	-2.18061700	C	3.98548000	-3.19020600	-1.64209400
C	2.92318500	-3.98504600	-1.20438700	C	1.61265000	-3.51887000	-1.30238300
H	0.78901900	-4.14804300	-0.97128900	H	3.11523900	-4.97195000	-0.79176500
H	5.00653800	-3.55455700	-1.56890200	H	4.54590500	-1.30723600	-2.53146200
H	2.21856500	-0.48636200	-2.70916600				

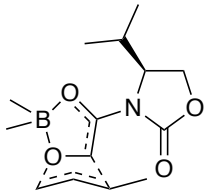
Table A.3.13. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_A}$.

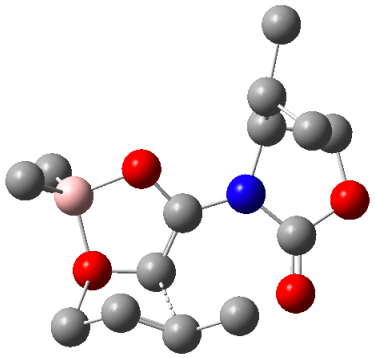


G = –928.130041 Hartree
G_{MP2} = –580544.4903 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.06876800	0.18547700	0.11509200
H	-0.16887400	-0.57744417	-0.91630091	C	-0.86190609	1.28424800	0.04148874
H	-1.23589891	1.53294591	-0.95056626	C	-0.16466417	2.53231700	0.63890391
H	-0.95111826	3.29719500	0.71306583	C	0.41546774	2.30531109	2.03953891
H	0.84611766	3.23489209	2.42183491	H	-0.35145626	1.98075600	2.75280991
H	1.21531183	1.54961909	2.04086700	C	0.89648683	3.05613509	-0.33858200
H	1.72321783	2.34970317	-0.46441200	H	0.46725783	3.25804017	-1.32818600
H	1.32438374	3.99277409	0.03318509	N	-1.97532217	0.78888591	0.86411857
C	-3.16126000	1.47164991	1.01191040	C	-4.18366360	1.28043891	1.94827131
H	-4.18079326	0.58942291	2.77937140	O	-5.09894997	2.22144103	1.84242278
B	-4.56546809	3.31414834	0.85825469	O	-3.35816657	2.50276043	0.24410934
C	-5.58101309	3.75789291	-0.29838548	H	-5.13166652	4.54891817	-0.91901557
H	-5.87786483	2.94969074	-0.97385131	H	-6.50173934	4.18938648	0.12825860
C	-3.97287366	4.50943378	1.76795991	H	-3.46254874	5.26788760	1.16025166
H	-4.78172357	5.01957486	2.30972900	H	-3.25954857	4.15496495	2.52449891
C	-7.02105914	1.05609828	0.99981445	C	-6.27384621	0.25206583	0.16747591
H	-6.22620295	0.50470731	-0.89324726	C	-5.41462222	-0.74605997	0.63665569
H	-5.52100009	-1.06097540	1.67371852	C	-4.63765114	-1.65891488	-0.26148440
H	-5.17568274	-2.61461053	-0.37739109	H	-4.50038162	-1.23354953	-1.25802314
H	-3.65851840	-1.91399983	0.16337478	H	-7.10521490	0.81997691	2.06551440
H	-7.57432288	1.91241028	0.63416102	C	-1.65445809	-0.38894100	1.53939791
O	-0.43474909	-0.80271091	1.11815709	O	-2.31988109	-0.96241674	2.36861009

Table A.3.14. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_B}$.

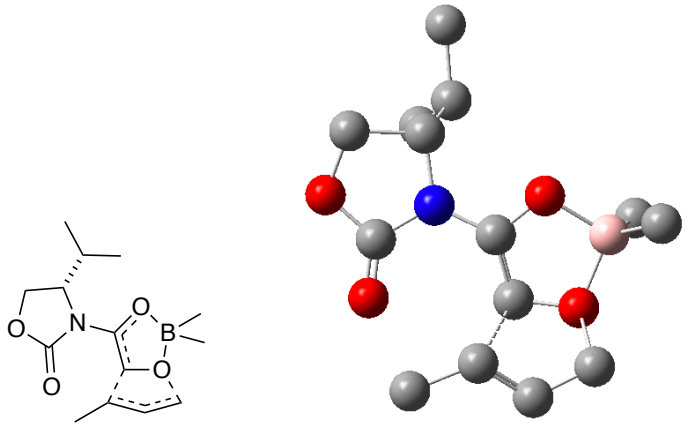




G = –928.12871 Hartree
G_{MP2} = –580542.881 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.93522500	-0.07646100	0.55591800
H	0.17443100	0.56314000	-0.92277700	C	-1.16422300	0.58674800	0.82861200
H	-1.39998300	1.60426800	0.50375700	C	-0.94902300	0.60340400	2.36143600
H	-1.91455600	0.90154500	2.78525800	C	0.08056900	1.68148400	2.73396700
H	0.17100700	1.76307000	3.82231900	H	1.07959700	1.44855700	2.34284100
H	-0.21089400	2.66621000	2.34960200	C	-0.57043400	-0.76518800	2.94365400
H	0.40319900	-1.11653500	2.57997000	H	-0.50522500	-0.70287700	4.03549700
H	-1.31596400	-1.52939600	2.70180100	N	-2.24483100	-0.31020100	0.38970200
C	-1.75924200	-1.45057400	-0.24012300	O	-0.41047300	-1.33509600	-0.35765300
O	-2.39077000	-2.40658500	-0.62424100	C	-3.59086700	-0.00622300	0.52149500
C	-4.67389900	-0.60790500	-0.08344200	H	-4.67879100	-1.41313000	-0.79955500
O	-5.81701100	0.02142100	0.25607000	B	-5.36635300	1.41375100	0.92290900
O	-3.89253700	1.04442500	1.24942400	C	-5.40216400	2.51539400	-0.25431300
H	-6.43065000	2.70400800	-0.58941400	H	-4.99890600	3.47485300	0.09731300
H	-4.82300400	2.21858400	-1.13923100	C	-6.17258300	1.78127000	2.25695400
H	-7.24324200	1.92577600	2.05772700	H	-6.07605600	1.03817400	3.05851400
H	-5.80558300	2.73403200	2.66214000	C	-6.93687700	-1.23394100	1.45234700
H	-7.26997400	-1.73924400	0.55226300	H	-7.61669200	-0.49292800	1.85371000
C	-5.94944400	-1.81930500	2.25740800	C	-5.05809900	-2.72446900	1.74285800
H	-5.26812700	-3.16302800	0.76963700	C	-3.89313400	-3.30139300	2.48074900
H	-3.00014000	-3.30345000	1.84626500	H	-3.67943500	-2.75366000	3.40437800
H	-4.08733300	-4.35167700	2.74585200	H	-5.76020400	-1.39316000	3.24138900

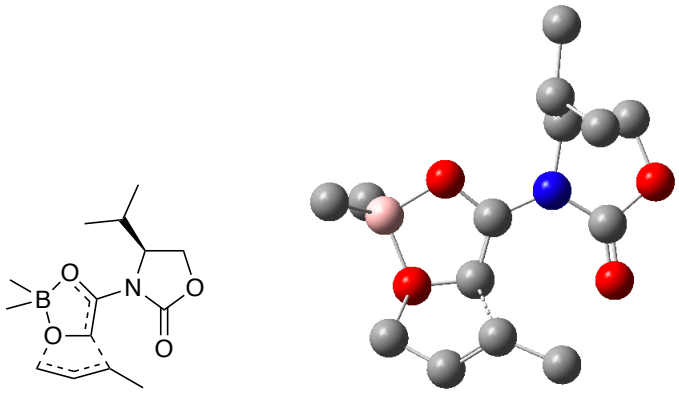
Table A.3.15. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21}_{\mathbf{C}}$.



G = –928.127504 Hartree
G_{MP2} = –580539.5605 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.07223500	0.04612100	0.19475800
H	-0.16699000	-0.42593900	-0.99503600	C	-0.71777100	1.35514400	0.17943600
H	-0.98915000	1.78152400	-0.78996100	C	0.05816400	2.42357900	0.98700000
H	-0.64700300	3.25119500	1.12684200	C	0.50588100	1.93850700	2.37334800
H	1.22447300	1.11189200	2.31125600	H	0.99504600	2.75547800	2.91472000
H	-0.34130200	1.60502100	2.98189700	C	1.23943300	2.95471700	0.16047900
H	1.73556500	3.77557800	0.68898700	H	1.99730500	2.18114700	-0.01979600
H	0.90977300	3.33717800	-0.81290600	N	-1.93722700	0.88782500	0.85763500
C	-3.06030100	1.68259200	1.03042500	C	-4.15038500	1.48656300	1.85463000
H	-4.30057000	0.70966100	2.58444200	O	-5.01329100	2.51797300	1.74729900
C	-6.79854200	1.86114800	0.80112500	H	-7.47036400	2.47169300	1.39336500
H	-6.46831900	2.28991400	-0.13456000	C	-6.70469100	0.48093200	1.01352000
H	-7.23212800	0.04184100	1.85991500	C	-5.78303200	-0.28467500	0.34544500
H	-5.26172900	0.16246700	-0.49989000	C	-5.54107200	-1.73860700	0.59830600
H	-6.14712100	-2.10793700	1.43180400	H	-5.78614100	-2.33170300	-0.29487100
H	-4.48848800	-1.92738700	0.83472800	B	-4.21879500	3.67491300	0.97639500
O	-3.08856100	2.80854000	0.35396600	C	-5.05942000	4.40832900	-0.17700700
H	-5.27848000	3.77499900	-1.04712800	H	-6.01199500	4.80736800	0.19649400
H	-4.49181800	5.26871600	-0.55582700	C	-3.60338900	4.63832000	2.11586300
H	-2.94140200	5.39491400	1.67253400	H	-4.39768000	5.18044100	2.64610900
H	-3.02437800	4.09351400	2.87403600	C	-1.78488000	-0.38791600	1.38525300
O	-0.58853800	-0.88423700	0.97398000	O	-2.55572500	-0.99003700	2.09512900

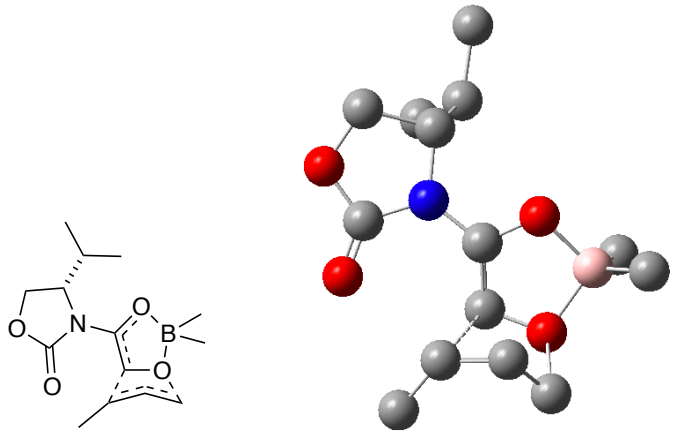
Table A.3.16. Geometric coordinates and thermally corrected MP2 energies for transition structure $\mathbf{21_D}$.



G = –928.127379 Hartree
G_{MP2} = –580539.744 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.92560700	0.12885500	0.56242200
H	-0.22157600	-0.50096800	-0.94818000	C	1.10959700	-0.72292500	0.79379600
H	1.25166900	-1.74330900	0.42727700	C	0.90507600	-0.77779200	2.32759500
H	1.83474900	-1.19833900	2.72792300	C	-0.23402700	-1.74875400	2.67411300
H	-0.31955100	-1.86475000	3.75977700	H	-1.20538400	-1.39027700	2.30948800
H	-0.05879700	-2.74296700	2.24610900	C	0.68795400	0.60224500	2.96480100
H	-0.23768500	1.07757700	2.61822700	H	0.61629600	0.50588300	4.05369000
H	1.51712600	1.28455400	2.74877100	N	2.26336100	0.09353500	0.38765000
C	1.87689000	1.30460900	-0.17338300	O	0.52347200	1.31053300	-0.29372300
O	2.58621100	2.22444900	-0.50644500	C	3.57846900	-0.32172500	0.53480800
C	4.73573200	0.28120800	0.08873300	H	4.83595300	1.16981200	-0.51036600
O	5.80970800	-0.48453900	0.38332200	B	5.21963800	-1.91877500	0.79740200
O	3.76273500	-1.48549600	1.11828300	C	5.23961800	-2.81829800	-0.54154000
H	4.74281200	-2.33425800	-1.39311000	H	6.26932200	-3.04052000	-0.85161700
H	4.74098300	-3.78223500	-0.37160000	C	5.90950800	-2.57366700	2.08948800
H	6.99985200	-2.64876900	1.98119000	H	5.70190800	-2.04615000	3.03038600
H	5.54195200	-3.59993600	2.22267100	C	6.97810800	0.45802000	1.84305000
C	6.55046100	1.78657300	1.70937900	C	5.30228100	2.17626100	2.11948400
H	4.72877200	1.48869000	2.73974300	C	4.71255600	3.53119500	1.88941200
H	5.39145000	4.17363800	1.31952200	H	3.77032800	3.45752400	1.33500900
H	4.49054200	4.02588800	2.84593000	H	7.13300700	2.46693400	1.08888800
H	7.93465400	0.13974400	1.44480200	H	6.55505300	-0.17034500	2.61429400

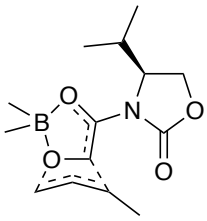
Table A.3.17. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from favor face forming anti product.

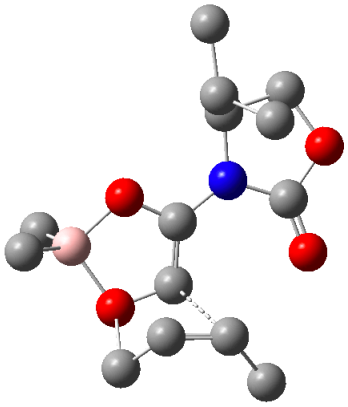


G = –928.119238 Hartree
G_{MP2} = –580536.7388 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	1.06873000	0.06331300	0.20930300
H	-0.14462800	-0.35814100	-1.02469400	C	-0.75824100	1.31913100	0.26631000
H	-1.05135500	1.79404600	-0.67375100	C	-0.00890600	2.36174500	1.13064500
H	-0.73433300	3.16360200	1.31373700	C	0.44870300	1.81187300	2.48923900
H	0.92486700	2.60645900	3.07387700	H	-0.39286700	1.43194300	3.07794400
H	1.18054100	1.00137100	2.38290800	C	1.16001400	2.96526000	0.33707200
H	1.94079100	2.22273600	0.12718700	H	0.82455200	3.38247700	-0.61990500
H	1.62893000	3.77479900	0.90626700	N	-1.95606500	0.77738400	0.92498900
C	-3.10789300	1.51968000	1.13597900	C	-4.16321500	1.26285700	1.98422900
H	-4.27982400	0.45131000	2.68266100	O	-5.09010600	2.23764900	1.89933800
B	-4.36257800	3.45502900	1.13698200	O	-3.20511700	2.65570900	0.48244700
C	-5.26807700	4.16039900	0.01919000	H	-4.70311600	4.97689800	-0.45052400
H	-5.58616100	3.49146300	-0.79053400	H	-6.16750500	4.61996500	0.45133100
C	-3.78018400	4.42515100	2.28736800	H	-3.17672900	5.23122600	1.84773800
H	-4.59179100	4.90490600	2.85023600	H	-3.14900800	3.89927000	3.01663600
C	-6.78762400	1.49016000	0.95494200	C	-6.18931900	0.65191600	0.00381500
H	-5.95683600	1.08957300	-0.96473500	C	-5.63540000	-0.57021400	0.29479700
C	-5.91003100	-1.44665700	1.47876800	H	-6.49651500	-2.32029200	1.15628100
H	-4.97445100	-1.82675900	1.90054600	H	-6.47304000	-0.94326100	2.26895200
H	-5.04093400	-1.04113900	-0.48784200	H	-7.14184100	1.10009600	1.90155100
H	-7.20381400	2.44440600	0.65972400	C	-1.77878300	-0.53375300	1.34521400
O	-0.57011800	-0.96919400	0.90110600	O	-2.53812400	-1.20984300	1.99822700

Table A.3.18. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from nonfavor face forming anti product.



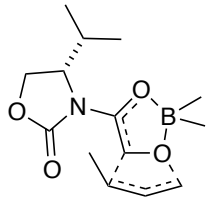


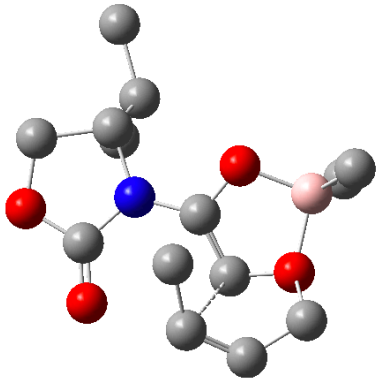
G = –928.118502 Hartree

G_{MP2} = –580536.5739 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-0.91083400	0.06307200	0.59677900
H	-0.24386000	-0.40011300	-0.98972100	C	1.13205800	-0.79535600	0.68528400
H	1.26089400	-1.77464500	0.21551500	C	0.97142600	-1.00208600	2.21143200
H	1.90708100	-1.46750100	2.54056200	C	-0.16847000	-1.99299700	2.49340400
H	-0.21944800	-2.22069700	3.56342800	H	-1.14674300	-1.58974700	2.20150300
H	-0.02070200	-2.93919800	1.95934900	C	0.78908000	0.30877300	2.99024200
H	-0.13397800	0.83271300	2.71297100	H	0.73568800	0.10162600	4.06470000
H	1.62696600	0.99577500	2.82924500	N	2.27207300	0.06080800	0.32460200
C	1.86724900	1.32634200	-0.08163900	O	0.51088100	1.33741600	-0.16642600
O	2.56365000	2.28337800	-0.32407200	C	3.59486400	-0.33914200	0.43437400
C	4.73475300	0.31218100	0.01495500	O	5.82971800	-0.43096000	0.27398200
B	5.27686600	-1.91100300	0.59017200	O	3.81169600	-1.53418900	0.93698500
C	5.31986500	-2.71745300	-0.80621700	H	4.86182500	-3.70982700	-0.69583900
H	4.79420100	-2.20028200	-1.62005900	H	6.35389900	-2.87773600	-1.13895600
C	5.99283900	-2.62529100	1.83243000	H	7.06584200	-2.77734500	1.65236200
H	5.88280700	-2.09437500	2.78665600	H	5.56346600	-3.62585400	1.97773100
C	6.90889600	0.44895800	1.80402800	H	7.39212200	1.10395000	1.08900400
H	7.47583800	-0.42802700	2.08819400	C	5.86324300	0.91140400	2.61698800
C	5.09470900	2.01171900	2.32987000	C	5.42515400	3.15743200	1.42207700
H	4.57609400	3.39037900	0.77168900	H	5.62439200	4.05537000	2.02624400
H	6.30410800	2.97576800	0.79832900	H	4.20468900	2.16299000	2.94086300
H	5.50493200	0.23825400	3.39296700	H	4.82054800	1.25498400	-0.49814300

Table A.3.19. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from favor face forming syn product.



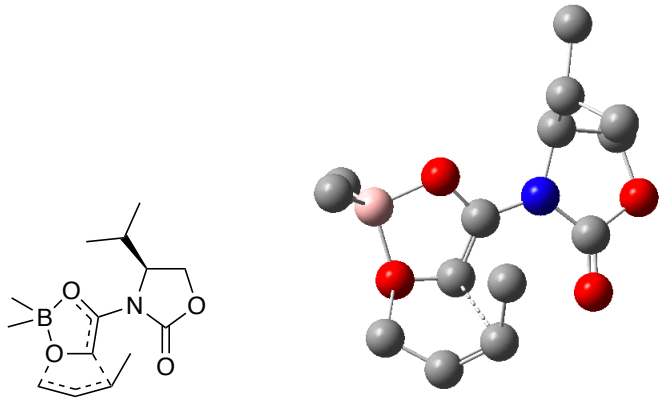


G = –928.11662 Hartree

G_{MP2} = –580534.9285 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	-1.06765400	0.14360300	-0.17268400
H	0.14392900	-0.47578400	0.97603600	C	0.82659800	1.29845400	-0.13848600
H	1.16755700	1.64571800	0.84051800	C	0.12013500	2.47365800	-0.85521700
H	0.88631800	3.25086900	-0.96555200	C	-0.39769600	2.11300800	-2.25462600
H	-1.17471900	1.33932600	-2.22199600	H	-0.83717200	2.99623600	-2.73061000
H	0.40730700	1.75648600	-2.90558800	C	-0.99395600	3.04380400	0.03618400
H	-0.61252200	3.33141700	1.02326900	H	-1.43165400	3.93605900	-0.42378500
H	-1.80906000	2.32385800	0.18577400	N	1.97594300	0.77097500	-0.88839900
C	3.15703700	1.47376000	-1.06726400	C	4.15777200	1.25557300	-1.98161900
H	4.19414800	0.52748600	-2.77319400	O	5.16814100	2.13939200	-1.80136800
C	6.82806100	1.19786600	-1.06719100	H	7.52130600	1.70873700	-1.72524500
H	6.72771300	1.62467300	-0.08011500	C	6.50076600	-0.15090200	-1.30730500
H	6.80902200	-0.57862800	-2.25975700	C	5.60019000	-0.86337800	-0.56193400
H	5.29906800	-1.83712800	-0.94508100	C	5.08480800	-0.53269300	0.80536100
H	5.62458500	-1.12566200	1.55933900	H	5.18598000	0.52267500	1.06836400
H	4.02734100	-0.80625000	0.89484100	B	4.53723100	3.30466000	-0.87333800
O	3.36053900	2.50413300	-0.26974300	C	5.52024900	3.83201000	0.27869400
H	6.47893500	4.18259600	-0.12645200	H	5.06471400	4.69513000	0.78227200
H	5.73703000	3.09636500	1.06556300	C	3.98844400	4.42948600	-1.89179100
H	3.44488100	5.21340400	-1.34668300	H	4.81436400	4.92329100	-2.42066700
H	3.31086600	4.02626100	-2.65632300	C	1.71795500	-0.47683800	-1.44411000
O	0.49555300	-0.89295000	-1.01527100	O	2.42631000	-1.11472300	-2.18523700

Table A.3.20. Geometric coordinates and thermally corrected MP2 energies for transition structure of **1g** rearranging from nonfavor face forming syn product.



G = –928.116483 Hartree
G_{MP2} = –580534.3017 kcal/mol

C	0.00000000	0.00000000	0.00000000	H	0.95022300	-0.04400600	0.53374000
H	0.16951300	0.40155500	-1.00480600	C	-1.09891600	0.77619800	0.75722200
H	-1.27595600	1.75252000	0.29658500	C	-0.83964600	0.99083900	2.26815100
H	-1.78030300	1.38318100	2.67049900	C	0.24192400	2.06443600	2.46564000
H	0.38185300	2.27478400	3.53130700	H	1.21435100	1.74528200	2.06803000
H	-0.03100700	3.00531300	1.97344600	C	-0.49204900	-0.29959600	3.02406400
H	-1.26023600	-1.06934900	2.89569800	H	0.46511300	-0.72461500	2.69878300
H	-0.40853900	-0.09402300	4.09684500	N	-2.24676500	-0.09733900	0.46813100
C	-1.85059300	-1.35242900	0.01581200	O	-0.49730700	-1.34664600	-0.12881200
O	-2.55024100	-2.30898500	-0.21309800	C	-3.56725100	0.31424500	0.56164600
C	-4.68709100	-0.27474700	0.02739400	H	-4.74974400	-1.15762100	-0.58519300
O	-5.79185800	0.45519300	0.30781300	B	-5.23436000	1.88293100	0.81951500
O	-3.79577600	1.44990400	1.19067900	C	-5.20975400	2.83806400	-0.47999600
H	-4.66134800	2.40056400	-1.32488600	H	-6.22693900	3.05528500	-0.83178600
H	-4.73938900	3.80239800	-0.24413700	C	-6.00145200	2.46588600	2.10174000
H	-7.08064500	2.56847800	1.92592200	H	-5.86528600	1.87797600	3.02008600
H	-5.62874300	3.47470200	2.32430600	C	-7.04390000	-0.56629700	1.57203500
C	-6.49041800	-1.85898600	1.50193200	C	-5.32468300	-2.22314700	2.12060900
H	-4.90448700	-3.19308300	1.86004700	C	-4.62850200	-1.50371500	3.23486500
H	-3.54315000	-1.61549800	3.14321600	H	-4.85866400	-0.43646400	3.27472900
H	-4.90944100	-1.94904000	4.20159600	H	-6.88733800	-2.53395800	0.74561800
H	-7.94463400	-0.33597600	1.01491900	H	-6.84349000	0.08019400	2.41395600

Chapter 3 References and Footnotes

1. (a) Tomooka, K.; Komine, N.; Nakai, T. *Chirality* **2000**, *12*, 505. (b) Nakai, T.; Mikami, K. *Org. React.* **1994**, 46. (c) Knochel, P.; Molander, G. A. In *Comprehensive Organic Synthesis* (2nd Ed.), 2014, Vol. 3, p. 1038.

2. (a) Jermaks, J.; Tallmadge, E. H.; Keresztes, I.; Collum, D. B. *J. Am. Chem. Soc.* **2018**, *140*, 3077. (b) Tallmadge, E. H.; Jermaks, J.; Collum, D. B. *J. Am. Chem. Soc.* **2016**, *138*, 345. (c) Zhang, Z.; Collum, D. B. *J. Am. Chem. Soc.* **2019**, *141*, 388. (d) Zhang, Z.; Collum, D. B. *J. Org. Chem.* **2017**, *82*, 7595.

3. (a) *Modern Aldol Reactions*, Mahrwald, R., Ed.; Wiley-VCH: Weinheim, 2004, Vol. 1 and 2. (b) Lin, G.-Q.; Li, Y.-M.; Chan, A. S. C. *Principles and Applications of Asymmetric Synthesis*, Wiley & Sons: New York, 2001; p. 135. (c) Mahrwald, R. in *Aldol Reactions*, Springer: New York, 2009. (d) Evans, D. A.; Kim, A. S.; Skrydstrup, T.; Taaning, R. H. (S)-4-Benzyl-2-oxazolidinone. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons: New York, 2007, pp. 1-18.

4. For structurally similar carboxamide auxiliaries undergoing [2,3] sigmatropic rearrangements, see: Mikami, K.; Takahashi, O.; Kasuga, T.; Nakai, T. *Chem. Lett.* **1985**, 1729.

5. (a) Oh, T.; Wrobel, Z.; Rubenstein, S. M. *Tetrahedron Lett.* **1991**, *32*, 4647. (b) Fujimoto, K.; Nakai, T. *Tetrahedron Lett.* **1994**, *35*, 5019.

6. (a) Emmadi, N. R.; Bingi, C.; Kumar, C. G.; Yedla, P.; Atmakur, K. *Synthesis* **2014**, *46*, 2945. (b) Evans, D. A.; Adams, D. J.; Kwan, E. E. *J. Am. Chem. Soc.* **2012**, *134*, 8162. (c) Cowden, C. J.; Paterson, I. *Org. React.* **1997**, *51*, 1.

7. For other examples of physical studies of Evans enolates, see: (a) Shinisha, C. B.; Sunoj, R. B. *J. Am. Chem. Soc.* **2010**, *132*, 12319. (b) Sreenithya, A.; Sunoj, R. B. *Org. Lett.* **2012**, *14*, 5752. (c) Shinisha, C. B.; Sunoj, R. B. *Org. Lett.* **2010**, *12*, 2868. (d) Goodman, J. M.; Paton, R. S. *Chem. Commun.* **2007**, 2124. (e) Baringhaus, K. H.; Matter, H.; Kurz, M. *J. Org. Chem.* **2000**, *65*, 5031. (f) Kimball, D. B.; Michalczyk, R.; Moody, E.; Ollivault-Shiflett, M.; De Jesus, K.; Silks, L. A. III *J. Am. Chem. Soc.* **2003**, *125*, 14666.

8. Taillier, C.; Hameury, T.; Bellosta, V.; Cossy, J. *Tetrahedron* **2007**, *63*, 4472.

9. Crimmins, M. T.; King, B. W.; Zuercher, W. J.; Choy, A. L. *J. Org. Chem.* **2000**, *65*, 8499.

10. A more convergent synthesis based on alkoxide displacement of an α-bromoacetyl-containing oxazolidinone failed owing to competitive deacylation.

11. Liu, Q.; Xiong, F.-J.; He, Q.-Q.; Chen, F.-E. *Org. Process Res. Dev.* **2013**, *17*, 1540.

12. (a) Scheffler, U.; Mahrwald, R. *J. Org. Chem.* **2012**, *77*, 2310. (b) Akita, H.; Matsukura, H.; Oishi, T. *Chem. Pharm. Bull.* **1986**, *34*, 2656.

13. (a) Heidlindemann, M.; Hammel, M.; Scheffler, U.; Mahrwald, R.; Hummel, W.; Berkessel, A.; Groger, H. *J. Org. Chem.* **2015**, *80*, 3387. (b) Shimizu, T.; Hiranuma, S.; Nakata, T. *Tetrahedron Letters*, **1996**, *37*, 6145.

14. Rein, A. J.; Donahue, S. M.; Pavlosky, M. A. *Curr. Opin. Drug Discov. Dev.* **2000**, *3*, 734.

15. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

16. Stevens, J. M.; Parra-Rivera, A. C.; Dixon, D. D.; Beutner, G. L.; DelMonte, A. J.; Frantz, D. E.; Janey, J. M.; Paulson, J.; Talley, M. R. *J. Org. Chem*. **2018**, *83*, 14245.

17. Ozonolysis of **23** afforded an aldehyde characterized crystallographically. We thank Dr. Samantha N. MacMillan for her help.

18. Morgan, J. B.; Morken, J. P. *Org. Lett.* **2003**, *5*, 2573.

19. Adam, W.; Peters, K.; Peters, E.-M.; Schambony, S. B. *J. Am. Chem. Soc.* **2001**, *123*, 7228.